

Synthesis of Surfactant from Fatty Acid

by

Hanis Farhana Sakim

Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2005

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CERTIFICATION OF APPROVAL

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Chemical Engineering Programme

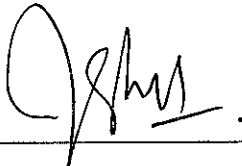
Universiti Teknologi PETRONAS

In partial fulfillment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

Approved by,



(ASSOC. PROF. DR. ISA MD. TAN)

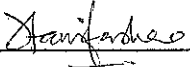
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CERTIFICATION OF ORIGINALITY

This is to verify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and the original work contain herein have not been undertaken or done by unspecified sources or persons.



(HANIS FARHANA BINTI SAKIM)

ABSTRACT

Oil is an important world resource which is limited. Demand of oil increased every day but conversely oil reservoirs keep depleted by day. This increasing demand make exploitation oil to a higher degree is desirable. Surfactants are believed can be a good second drive mechanism for enhance oil recovery since it has lower interfacial tension. There are lots of surfactants types but fatty acid surfactant is believed can be a good source for producing surfactant in Malaysia. This is because; palm oil which is source of fatty acids is environmental friendly and highly resource able in Malaysia. The scope of this research project is to synthesize surfactant from fatty acids, characterize their properties and compare it to commercial surfactants' properties. This surfactant is synthesized from palm cooking oil through purification process and saponification process. Purification process involves decolorization, deodorization, hydrolysis and distillation process whereas saponification process involves titration between purified oil with five different molarity of sodium hydroxides and potassium hydroxides. There are four experiment conducted to characterize and compare properties of synthesize and commercial surfactants. They are conductivity test, surfactants' effectiveness test, differential scanning calorimeter and dynamic mechanical analyzer. Conductivity test plot, differential scanning calorimeter plot and dynamic mechanical analyzer plot shows almost similar plot between synthesize and commercial surfactants either on conductivity trends, phase transition trends or modulus trend. This indicates they may have similar molecular agitecture. However, they are some significant differences between them such as its phase transition in differential scanning calorimeter, its modulus, viscosity or chemical bonding among the materials. This differentiation signifies commercial surfactant to have higher material degradability, higher interfacial tension and less modulus/viscous than synthesize surfactant. There are predicted additive added to commercial surfactant to have this significant properties. Thus, research must be continued to develop the surfactants from fatty acid which can attest to industrial applications.

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ABBREVIATIONS AND NOMENCLATURES

Bbbl	=	Billion barrel
CMC	=	Critical Micelle Concentration
DMA	=	Dynamic Mechanical Analyzer
DSC	=	Differential Scanning Calorimeter
ECD	=	Equivalent Circulating Density
EOR	=	Enhance Oil Recovery
GC	=	Gas Chromatography
HPLC	=	High Pressure Liquid Chromatography
IFT	=	Interfacial Tension
MW	=	Molecular Weight
M'	=	Young Modulus / Storage Modulus
M''	=	Loss Modulus
NaOH	=	Sodium Hydroxide
OIIP	=	Oil Initially In Place
ROP	=	Rate of penetration
RP-HPLC	=	Reverse Phase- High Pressure Liquid Chromatography
SPE	=	Society of Petroleum Engineers
T_c	=	Crystallization Temperature
T_g	=	Glass Transition Temperature
T_m	=	Melting Temperature

TABLE OF CONTENTS

CERTIFICATE OF APPROVAL.....	i
CERTIFICATION OF ORIGINALITY.....	ii
ABSTRACT.....	iii
ACKNOWLEDGEMENT.....	iv
NOMENCLATURE.....	v
TABLE OF CONTENTS.....	vi
LIST OF FIGURES.....	viii
LIST OF TABLES.....	ix
 CHAPTER 1: INTRODUCTION	
1.1 Background of Study.....	1
1.2 Problem Statement.....	1
1.3 Objective and Scope of Study.....	2
 CHAPTER 2: LITERATURE REVIEW / THEORY	
2.1 Surfactants: Synthesize Steps, Properties and Application in EOR.....	3
2.2 Literature on Sample Characterizations' Equipment.....	17
 CHAPTER 3: METHODOLOGY / PROJECT WORK	
3.1 Elements Determination.....	27
3.2 Sample Preparation.....	28
3.3 Sample Characterization and Comparison.....	31
3.4 Apparatus required.....	33

CHAPTER 4: RESULT / DISCUSSION
4.1 Results.....35
4.2 Discussion.....40

CHAPTER 5 CONCLUSION / RECOMMENDATION
5.1 Conclusion.....45
5.2 Recommendation.....46

REFERENCES.....47

APPENDICES.....49

LIST OF FIGURES

Figure 2.0: Hydrophobic and hydrophilic behaviour of surfactants

Figure 2.1: Oil sorbed into surfactant's molecule

Figure 2.3: Illustration of the physical property changes due to presence of surfactants

Figure 2.4: Illustrate relations between volumes of surfactant with cmc

Figure 2.5: Ternary Phase Diagrams on Evaluating Phase Behaviour of Surfactants

Figure 2.6: Intermolecular Forces as they affect Interfacial Tension

Figure 2.7: How the DuNouy Method Works

Figure 2.8: What Happen During the Interfacial Tension Test

Figure 2.9: DSC Schematic Diagram

Figure 2.10: DSC plot at beginning heat supply

Figure 2.11: DSC Plot when polymer change state from glass to rubbery state

Figure 2.12: Tangent construction for the determination of glass transition temperature

Figure 2.13: DSC plot at crystallization

Figure 2.14: DSC Plot at melting

Figure 2.15: DSC Plot

Figure 2.16: The stress-strain curve for an aluminium alloy

Figure 2.17: The force-distance curve for two materials

Figure 2.18: Complex modulus $|E^*|$, storage modulus E' , loss modulus E'' and loss tangent $\tan \delta$

Figure 2.19: High Pressure Liquid Chromatography

Figure 3.0: Steps in Purification Process

Figure 3.1: Steps in Saponification Process

Figure 3.2: Volume of base titrate for various molarity

Figure 4.0: Result of Conductivity Test Experiments

Figure 4.1: DSC Experimental Results for Synthesize Surfactant

Figure 4.2: DSC Experimental Results for Commercial Surfactant

Figure 4.3: DMA Young Modulus, M' Experimental Results for Synthesize Surfactant

Figure 4.4: DMA Young Modulus, M' Experimental Results for Commercial Surfactant

Figure 4.5: DMA Loss Modulus, M'' Experimental Results for Synthesize Surfactant

Figure 4.6: DMA Loss Modulus, M'' Experimental Results for Commercial Surfactant

Figure 4.7: DMA Tangents Delta, $\tan \delta$ Experimental Results for Synthesize Surfactant

Figure 4.8: DMA Tangents Delta, $\tan \delta$ Experimental Results for Commercial Surfactant

Figure 4.9: Result of Conductivity Test Experiments

LIST OF TABLES

Table 2.0: Surface Phase Types Description

Table 2.1: Differences of Relative Permeability and Self-selecting Plugging System

Table 4.0: Results of Surfactants' Effectiveness Experiment

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Surfactant is a compression of “**Surface active agent**”, which also known as wetting agents, lower the surface tension of a liquid, allowing easier spreading. This physical characteristic of surfactant is believed to enhance oil recovery even to sorbed organic compound to soil in the reservoir. In order to solve enhance oil recovery problems, surfactant is synthesized from fatty acid i.e. ester. Fatty acid is chose as an element for this surfactant because it is reliable to human, aquatic creatures, and environment.

The fatty acid is obtained from purification process of oil. In this process, oil is bleached, deodorized, hydrolysed and distilled. Hydrolysis process will break ester link into fatty acids and alcohol. The distilled fatty acid is then saponified through titration process with NaOH or KOH to produce surfactant.

1.2 PROBLEM STATEMENT

World oil resources are limited. Demand of oil increased every year. Thus, exploitation of oil fields to a higher degree is desirable. In USA, from 649 Bbbl original oil in place (OOIP), only 183 Bbbl was recovered cumulatively. A portion of 377 Bbbl of oil which trapped in mineral rock matrices are the target for improved recovery technologies. [1] Surfactant, which has capability to reduce interfacial tension, is believed can provide solution for enhancing oil recovery even to oil field which experienced trapped oil phases (residual saturation) or strongly sorbed organic compounds. [2] Thus, in this study, surfactant is synthesized from fatty acid since it is environmental friendly, highly resource able in Malaysia and applicable to oil field usage later.

1.3 OBJECTIVES AND SCOPE OF STUDY

The objectives of this study are:

1. To synthesis surfactant from fatty acids
2. To characterize synthesise and commercial surfactant and comparing their properties.

CHAPTER 2

LITERATURE REVIEW

2.1 SURFACTANTS: SYNTHESIZE STEPS, PROPERTIES AND ITS APPLICATION IN EOR

2.1.1 Definition of Surfactant

Surfactant is a compression of “**Surface active agent**”, which also known as wetting agents, lower the surface tension of a liquid, allowing easier spreading.

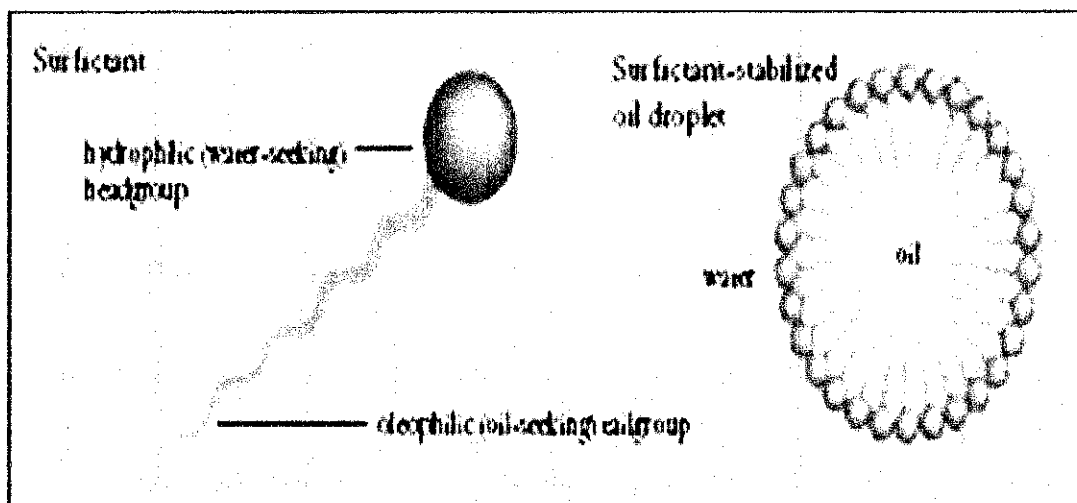


Figure 2.0: Hydrophobic and hydrophilic behaviour of surfactants

Surfactants are usually organic compounds that contain both hydrophobic (oleophilic) and hydrophilic groups, and are thus semi-soluble in both organic and aqueous solvents (Figure 2.0). Surfactants are also known as amphipathic compounds, meaning that they would prefer to be in neither phase (water or organic). For this reason they locate at the first boundry between the organic and water phase, or, if

Surfactants are active in:

- #### 2.1.1.1 How Surfactant's Work

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{O}^-\text{Na}^+$$

nonpolar **polar**

(dissolves in oils) (dissolves in water)

1. Surfactant adsorbing at oil/water interface

2. Oil dispersed into surfactant stabilized droplets

4

2.1.2 Synthesize of Surfactant

Two major processes are involved in synthesis of surfactant from fatty acid. They are:

1. Purification process
2. Saponification process

2.1.2.1 Purification Process

Purification process of oil is done to obtain ester for saponification process.

The processes involve four pre-steps with following objectives:

1. To bleach oil colour
2. To remove oil odour
3. To separate ester from oil
4. To distilled ester from its contaminants

2.1.2.1.1 Bleaching Oil Colour

Hydrogen peroxide is used in bleaching oil colour. In this process, oil will be boiled until 70°C. Hydrogen peroxide is added slowly to the under air agitation for one hour. The mixing oil and hydrogen peroxide is stir until three hours. The reaction between the hydrogen peroxide and oil will bleach the oil colour. [4]

2.1.2.1.2 Deodorization

Deodorization is done using activated carbon. In this process charcoal will be placed near the bleached oil until it absorbs the oil odour.

2.1.2.1.3 Hydrolysis Process

Hydrolysis is a chemical process in which a molecule is cleaved into two parts by the addition of a molecule of water. In a hydrolysis reaction that involves breaking an ester link, one hydrolysis product contains a hydroxyl functional group, while the other contains a carboxylic acid functional group. [5]

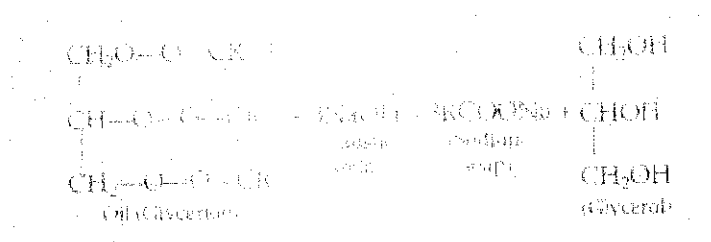
Hydrolysis takes place when high pressure and temperature steam cleaves the treated oil and water continuously. This hydrolysis process will break ester link from the treated oil into fatty acids (carboxylic acid) and alcohol (hydroxyl functional group).

2.1.2.1.4 Distillation of ester from oil contaminants.

The fatty acids and alcohol achieve from hydrolysis process is distilled using set-up distillation method practice in laboratory. At this stage, ester i.e. fatty acid practicable for saponification process is obtained.

2.1.2.2 Saponification Process

Saponification is reaction of a fat or a fatty acid with a base to produce soap. [6] Saponification also known as hydrolysis of an ester in aqueous NaOH or KOH to an alcohol and sodium and potassium salt of carboxylic acid. Saponification is an exothermic reaction liberating approximately 65 calories per kilogram of oil saponified.



In the above equation, R can represent the same or different fatty chains which may be designated as R1, R2 and R3 etc. These can be derived from lauric, oleic, palmitic, stearic or other acids which are the normal constituents present in the oil as glyceride esters. The actual glyceride structure would depend on the composition of the oil. Oils are mixtures of several glycerides whose proportions are determined by fatty acid composition of the respective oils. [4]

2.1.3 Properties of Surfactant

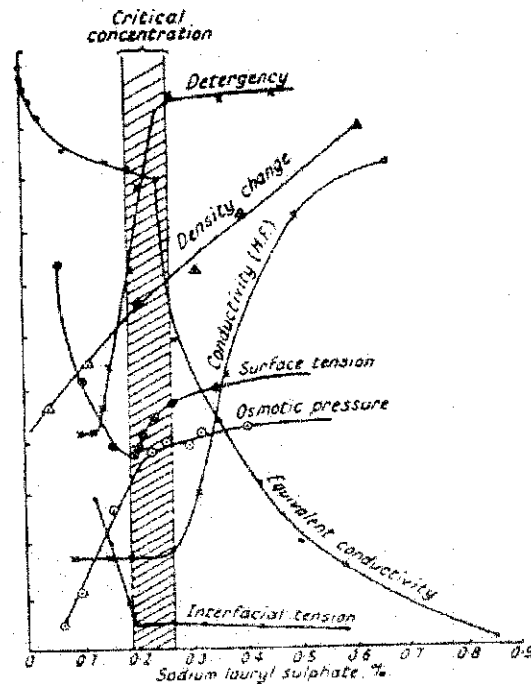


Figure 2.3: Illustration of the physical property changes due to presence of surfactants

2.1.3.1 Critical Micelle Concentration (CMC)

Critical Micelle Concentration or CMC is defined as the critical concentration whereby the molecular aggregates termed micelles are formed [6]. The cmc is a property of the surfactant. Significance of cmc can be explained the concept of micellar parameters. Formation of micelles is due to the formation of organized aggregates of large numbers of molecules, where lipophilic parts of the surfactants associate in the interior of the aggregate leaving hydrophilic parts to face the aqueous medium. CMC is one of the most important parameters because at concentrations above this value the adsorption of the surfactant onto reservoir surfaces increases very little. It represents the solution concentration of surfactant from which nearly maximum adsorption occurs.

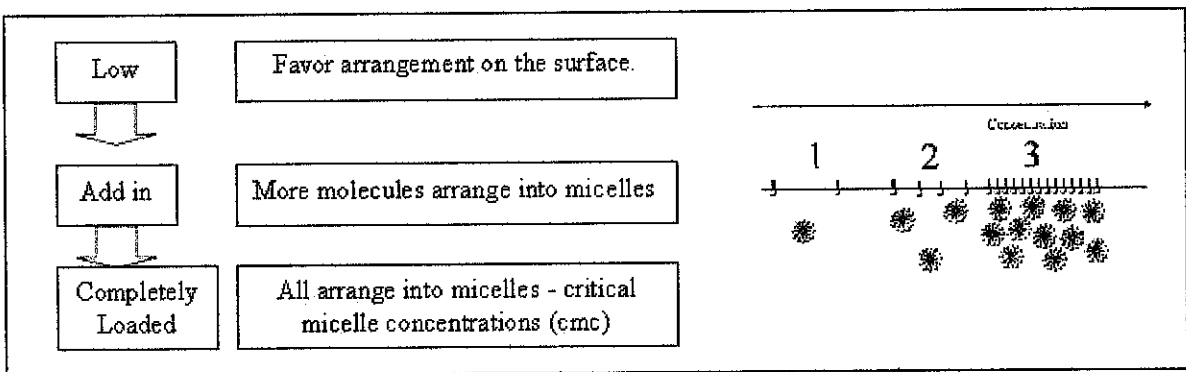


Figure 2.4 Illustrate relations between volumes of surfactant with cmc

2.1.3.2 Phase Behaviour

Phase Behaviour in surfactant property evaluation is normally represented by phase diagrams. These diagrams are used to explain the behaviour of surfactant systems. A typical diagram that is used is ternary phase diagram, which associates three different components, which are surfactant, brine and oil. In reservoir ternary diagrams, the components represented no longer true portray true thermodynamic components since they are in mixture forms. A crude oil contains hundreds of components, and the brine and surfactant pseudo components may also be complex mixtures. The ternary diagram shows the best representation of the phase behaviour and it is reasonably accurate as long as each component has approximately the same composition in each phase. In evaluating phase diagrams, phase behaviour type descriptions are used. Usually, it is classified according to physical observation of the mixture and crude oil.

The classifications of phase types are tabulated in the following:

Table 2.0: Surface Phase Types Description

Phase Type	Phase Type Description
II	Two fluid envelopes exist - a bottom aqueous phase and top oil phase. Color is not visible in the aqueous phase. The crude oil and aqueous phase are equal to the volumes placed in the tube. No crude oil swelling has taken place
II-	Two fluid envelopes exist, which comprises of bottom aqueous phase and an oil phase. The bottom aqueous phase is colored indicating the alkali has saponified acids in the crude oil which is present in the aqueous phase.
III	Three or more fluid envelopes exist, which comprises of bottom aqueous phase, middle emulsion phases, and top crude oil phase.
II+	Two fluids envelopes exist, where a bottom aqueous phase and a top crude oil phase are present. The bottom aqueous phase is clear because the surfactant reside in the crude oil phase.

According to Table 2.0, type III is the desired phase type to recover additional oil followed by type II-, II+ and type II. This is explained by the presence of interaction between the aqueous phase, crude oil and saponified acids. The relation to ternary phase diagrams explains the equilibrium interaction between of the three

major components. Type II- phase behaviour refers to the lowest salinity or lowest brine content in the solution. This is because most of the brine water is dissolved in the surfactant, interpreting that the surfactant is water soluble. Should the salinity increases, the surfactant would be more oil soluble, making the phase behaviour to be in the type III region, where the phases are distinguished by the top oil phase, middle emulsion phase, and bottom aqueous phase. Increasing the salinity changes the phase behaviour, and transforming the solution to be in the region of type II+. Here, it can be concluded that the surfactant is oil soluble, where most oil is dissolved in surfactant and in form of microemulsion followed by brine water. From the phase behaviour explanations, type III verifies as the most desired phase behaviour that the evaluations trying to achieve because it shows balanced interaction with the brine and the oil. It is also the target characteristics within the chemical flooding, where the main target is to minimize surfactant losses, and minimize oil solubility to the surfactant so that separation between the oil and the surfactant is easier and economically feasible.

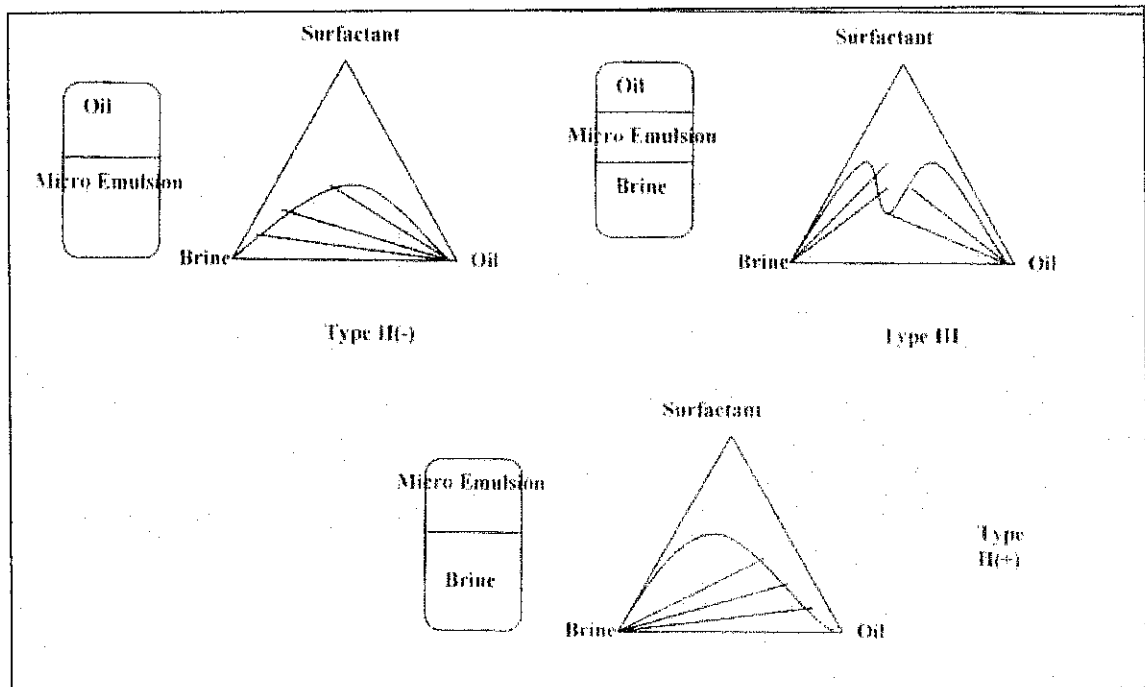


Figure 2.5: Ternary Phase Diagrams on Evaluating Phase Behaviour of Surfactants

For surfactant adsorption in porous media, this phenomenon can be described as the electrostatic interaction, Van der Waals interaction, hydrogen bonding and salvation and desolvation of adsorbate and adsorbant species. Normally it is a common

effect for the surfactant to be adsorbed onto solid surfaces specifically to the porous media, either on the walls of pores or fine particles in rock pores. In EOR, adsorption constitutes a loss of valuable surfactant and it directly affects the economic success of the flooding process. Thus, adsorption study is considered important so that the factors that influence adsorption and its consequences can be identified and acknowledged. From there, preventive measures by altering the properties or introduce inhibition of the surfactant could be done to minimize adsorption on the porous rocks, while maintaining its recovery efficiency. Through analysis, factors that influence adsorption are temperature, brine salinity and hardness, solution pH, rock type, wettability, and the presence of a residual oil phase. [6]

2.1.3.3 Interfacial Tension/ Surface Tension

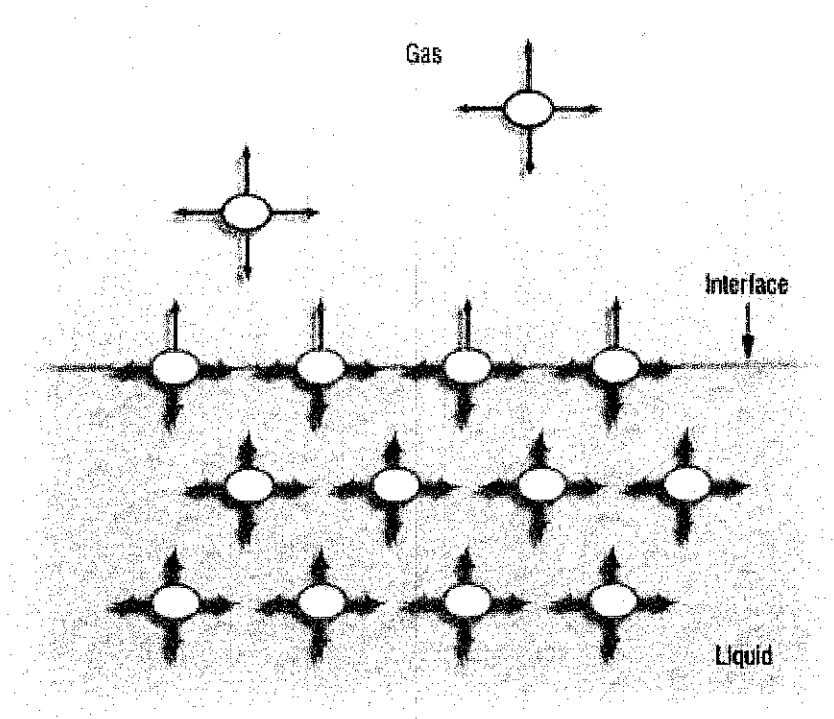


Figure 2.6: Intermolecular Forces as they affect Interfacial Tension

What is surface tension? Consider the layer of molecules on an oil’s surface that are in contact with air. As seen in Figure 2.6, the molecules are more strongly attracted from below because the molecules in the air are on average further apart (the attraction is inversely proportional to the distance between the molecules). A similar imbalance occurs between two immiscible liquids such as oil and water; in this case the phenomenon is called interfacial tension. At the air-oil interface, this imbalance

creates a skin-like membrane at the oil's surface causing the oil to want to form the smallest possible surface area. Due to the tendency of the surface to want to contract, it behaves as if it were in a state of tension. For the same reason, a drop of water falling through air tends to be spherical because a sphere has the minimum surface-to-volume ratio. [7]

Surface tension can be visualized by the contracting force at the surface, and it is due to the attractive Van der Waals forces between molecules are felt equally by all molecules except those in the interfacial region. This imbalance pulls the latter molecules towards the interior of the liquid. Surface tension is an important parameter because it displays the surface energy required for the foam formation to occur. It is desired for a surfactant to lower the surface tension as it would lead to lowering of the IFT, and at the same time less mechanical energy required for the formation of foam to occur within the oil. This is done by the expanding force acting against the normal interfacial tension. Interfacial tension is normally represented in terms of dynes/cm. Before the surfactant is injected within the reservoir, the normal IFT between the oil and rock is at 20 dynes/cm [6]. This is considered a large value because it results the binding of the oil and the water, making it trapped between the reservoir rocks, and consequently, limits the oil recovery capability. Introducing surfactants will tamper the normal interfacial tension of the oil and water, due to its interaction and propagation of oil, the surfactant reduces the IFT to the range of 0.002 dynes/cm [6]. At this range, this makes the oil recovery highly desirable, and surfactant is the main chemical component in chemical flooding.

2.1.3.3.1 Importance of surfactants' surface tension in oil recovery

In 1920's the use of surfactant to enhance oil recovery have so far met failure. However, interest in the technique has recently revived by several American petroleum companies, as witnessed by papers presented at the April 1972 SPE meeting in Tulsa. Most research workers consider that the primary cause of failure noted to date was that the interfacial tension was not reduced sufficiently to have an effect on the trapped oil.

It would appear that it is necessary to reduce the interfacial tension between the oil and the slug of surfactant-bearing water to the order of 0.01 to 0.001 dyn/cm and to be able to maintain this value for the duration of the displacement.

Laboratory studies have shown that the required large reduction in interfacial tension can only be achieved in a very narrow range of sodium chloride concentration (0.2 to 0.3 mole/litre). Thus it is necessary to inject water of suitable salinity before injecting surfactant solution. This pre-flush displaces the formation brine so that it is not come into contact with the surfactant solution.

In addition, various mineral additives are used with the surfactant slug to protect it against the formation water by the precipitation or sequestration of the divalent cations. The most popular additives are ammonia, sodium carbonate and sodium triphosphate. [8]

2.1.3.3.2 Measurement techniques in industry

The most common method of measuring surface/interfacial tension involves the use of a torsion balance known as the DuNouy instrument (tensiometer), described in ASTM D971:99a and ASTM D1331. In the test (Figures 2.7 and 2.8), the force required to lift a horizontal platinum wire ring away from the oil's surface is measured either directly (surface tension) or at an oil/water interface (interfacial tension). The unit of measure for surface tension is dynes per centimeter (equal to mN/m).

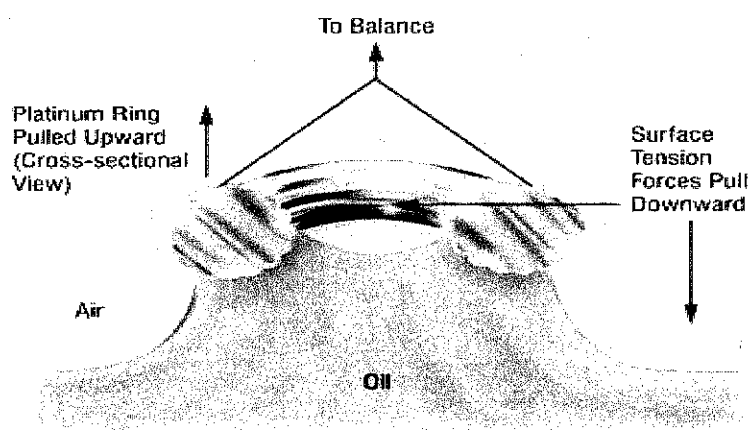


Figure 2.7: How the DuNouy Method Works

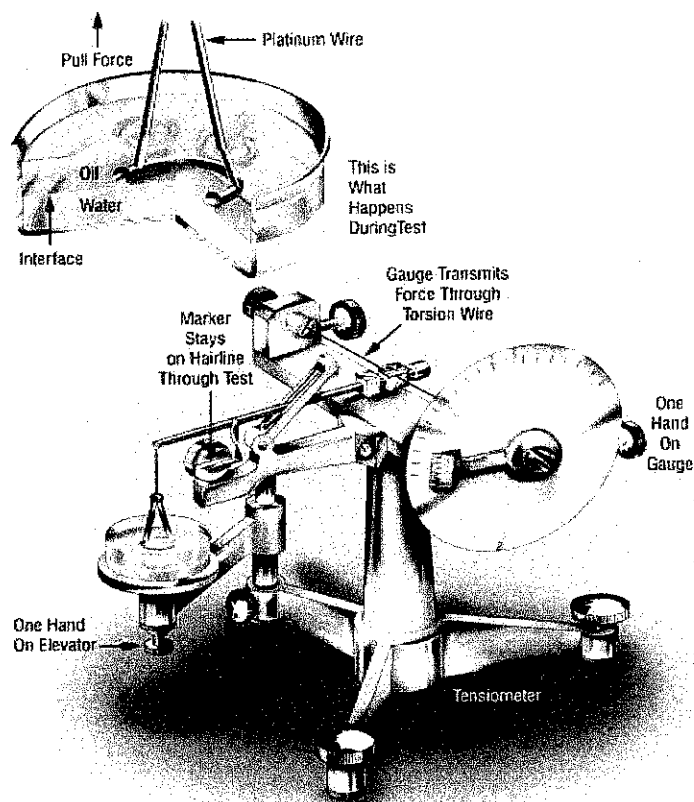


Figure 2.8: What Happen During the Interfacial Tension Test

Another method to determine interfacial tension is used to characterize the degradation of electrical insulating oils due to oxidation or contamination. It involves the use of a drop-weight procedure and is described in ASTM D2285:99. With any of the prescribed methods, test accuracy is affected by a number of factors including cleanliness of the test apparatus, agitation of the fluid (required to resuspend solids) and the accidental contamination of the fluid by dirty containers and laboratory glassware. In general, good reproducibility of these tests can be difficult to obtain unless care is taken to ensure quality lab test procedures. [7]

There are lot of equations to calculate the IFT, and generally it is a function of capillary pressure, adhesive forces between the oil and rock, and adhesion tension between oil-water and oil rock. Spinning drop method is usually applied in determining the IFT of the surfactants, and followed by the equation [6]:

$$IFT = (\text{Spinning Drop Constant}) (\text{Speed (ms/rev)})^{-2} (R_2 - R_1)^3 (\rho_s - \rho_c)$$

Where the

R_1 = Primary distance of elongated oil droplet

R_2 = Secondary distance of elongated oil droplet

$$\rho_s = \text{density of solution, (g/cm}^3\text{)}$$

$$\rho_c = \text{density of crude oil, (g/cm}^3\text{)}$$

2.1.4 Application of Surfactants in EOR

2.1.4.1 Introduction

Problems associated with water and gas production have triggered many companies, research institutions, and universities to study water- and gas-production problems and develop chemicals and mechanicals product that can control this problem.

Choosing the most suitable solution requires determining the cause of the water- or gas production problem. The problems can be reservoir scale, wellbore conditions, or capacity of surface production installation may demand a water- or gas-control treatment. A suitable solution can be achieved only if the problem has clearly been identified. Laboratory testing that compares the performance of systems can help identify the most suitable chemical solution for a particular situation.

2.1.4.2 Areas of Application

Application of chemical system for water and gas control can be classified into nonsealing and sealing system. Nonsealing systems restrict, but do not block, the flow of fluids and gases through a porous medium. Sealing systems can fully block the flow of fluids and gases through a porous medium.

2.1.4.2.1 Nonsealing systems

Nonsealing systems are typically diluted solutions of water-soluble polymers. These water-soluble polymer will reduce effective water permeability by adsorbs onto the formation, creating a layer of hydrated polymer along the pore throats. This layer reduces the effective radius of the pore throats, slowing fluid flow.

Example of commercially available chemical nonsealing systems are:

- Insitu-polymerized acrylate monomer
- Hydrophobically-modified, water-soluble polyacrylate
- Polyacrylamide and partially hydrolyzed polyacrylamide

Some nonsealing systems contain a base polymer and a crosslinker. These systems can react to create a “weak” gel that fills the pores of a porous medium, reducing the water permeability more than adsorbed polymers can. However, the reduction of the permeability to oil can also be larger than desired.

Most nonsealing polymer solutions can reduce the effective permeability to water more than the effective permeability to oil. This effect is called disproportional permeability reduction or relative permeability modification. A nonsealing system can be called a relative permeability modifier. This term should be distinguished from the term self-selecting plugging system. Table below summarizes the differences.

Table 2.1: Differences of Relative Permeability and Self-selecting Plugging System

Relative Permeability Modifier.	Self-Selecting Plugging System
Reduce relative permeability-to-water along the entire water saturation range	Reduce permeability of water at residual oil saturation. This system can reduce water flow only when water is flowing. Once oil is flowing, it will no longer influences fluid flow.

2.1.4.2.2 Sealing systems

Chemical sealing systems are porosity-fill materials that are best suited to a zone that can be mechanically or chemically isolated. Most chemical sealing systems rely on a crosslinking reaction between a base polymer and a crosslinker. Although some systems with a crosslinker behave like a relative permeability modifier, pumping such system without zonal isolation is risky because the pressure required to flow through the sealant may be too high for economic hydrocarbon production. Additionally, regained permeability after treatment can be 10 to 100 times less than initial permeability. This can be translated to a significant skin factor damage of oil-producing zone.

API cement has been the oldest sealing systems used in oil industry. The primary disadvantage of using cement is its large particle size and lack of penetration into matrix material. Introducing small particle size cements with particle size one-tenth the size of conventional API cement has increased the effectiveness of cement in

profile control. However, if the area of non-conformance lies deeper within reservoir, particulate plugging agents are not desirable.

Many sealing systems have been enhanced with either water- or hydrocarbon-based cement slurry as a tail-in to the chemical treatment. The use of hydrocarbon-based, small particle-sized cement has successfully shut off produced water when used as either a separate treatment or in combination with other sealing system. [9]

2.1.4.3 An example: ACCOLADE® system

ACCOLADE® system is newly developed emulsifiers and a polymeric filtration control agent which have capability to ensure plugging/sealing results are as good, if no better, than those achieved with conventional SBF fluids relying on clay and lignite.

The ACCOLADE® system, which is surfactant base application, can provide plugging/sealing characteristics across low permeable zones and micro-fractures without the use of clay or treated lignite. When drilling highly permeable zones, the plugging/ sealing properties of the ACCOLADE® system will be enhanced with the use of plugging/bridging agents such as BARACARB® calcium carbonate and STEELSEAL® resilient carbon coated graphite. Pre-treating the system with plugging/bridging agents does not alter the desirable rheology profile unique to this system. Below is its proved capability since its introduction in late 2001;

- ⇒ No evidence of barite sag – even after extended logging programs
- ⇒ Significantly reduced mud losses while drilling, running casing, and cementing – up to 80% less compared to offset wells.
- ⇒ Minimal gel spikes when breaking circulation after connections and trips
- ⇒ Stable rheological properties from 40°F to 350°F.
- ⇒ Better control equivalent circulating density (ECD), even at high flow rates
- ⇒ Fast rates of penetration (ROP)
- ⇒ Excellent suspension properties requiring fewer sweeps
- ⇒ High tolerance for contaminants [10]

2.2 LITERATURE ON SAMPLE CHARACTERIZATIONS' EQUIPMENT

2.2.1 Differential Scanning Calorimeter

Differential scanning calorimetry is a workhorse technique in many fields, particularly in polymer characterization. In a differential scanning calorimeter (DSC), heat flow into a sample—usually contained in a small aluminum capsule or 'pan'—is measured differentially, i.e. by comparing it to the flow into an empty reference pan.[11]. The DSC best pictured in Figure 2.9.

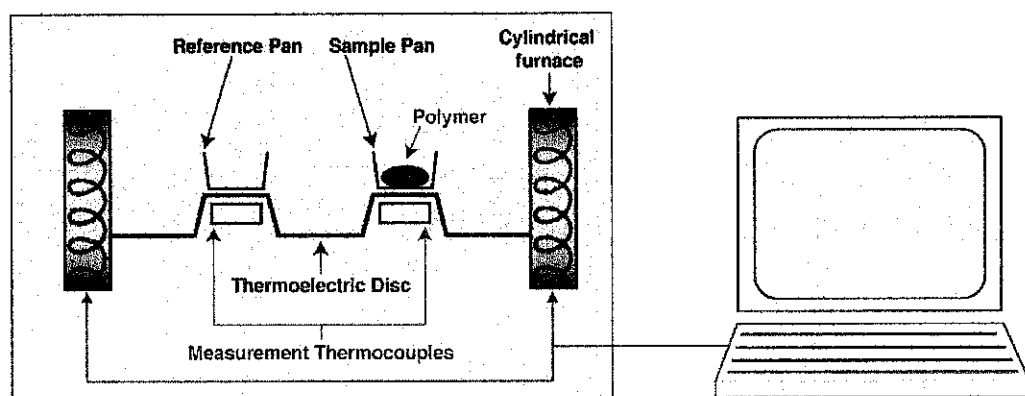


Figure 2.9: DSC Schematic Diagram

Sample and reference pans sit on a small slab of material with a known (calibrated) heat resistance K . The temperature of the calorimeter is raised linearly with time (scanned), i.e. the heating rate $dT/dt = \beta$ is kept constant. This time linearity requires good design and good (computerized) temperature control.

Heat flows into the two pans by conduction. The flow of heat into the sample is larger because of its heat capacity C_p . The difference in flow dq/dt induces a small temperature difference ΔT across the slab. This temperature difference is measured using a thermocouple. The heat capacity can in principle be determined from this signal:

$$\Delta T = K \frac{dq}{dt} = KC_p \beta$$

When a sudden change in the heat capacity occurs (e.g. when the sample melts), the signal will respond and exhibit a peak. From the integral of this peak the enthalpy of melting can be determined, and from its onset the melting temperature.

2.2.1.1 DSC Plot

During analyzing samples with reference, DSC will give a plot of heat flow versus temperature. Four important polymer characteristics can be analyzed from the plot i.e. heat capacity, glass transition temperature, crystallization and melting.

2.2.1.2 Heat Capacity

Specific heat capacity of a solid or liquid is defined as the heat required to raise unit mass of substance by one degree of temperature [12] i.e. $C_p = \frac{q}{\Delta T}$.

Obviously DSC plot of heat flow versus temperature will give us C_p .

2.2.1.3 Glass Transition Temperature, T_g

Glass transition temperature (T_g) is temperature at which the polymer transit from glass to rubbery state when it is heated. At low temperatures, this material indicates a glass-like behaviour within the glassy region and softens upon the application of heat into a toughened state. The glass transition state extends over a temperature range depending upon the type of plastics. Difficulties associated with measuring this material property have resulted in various methods for experimental determination. [12]

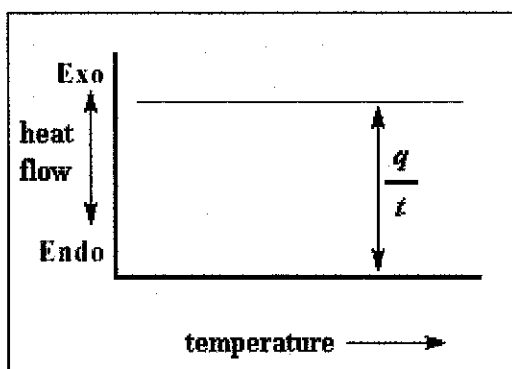


Figure 2.10: DSC plot at beginning heat supply

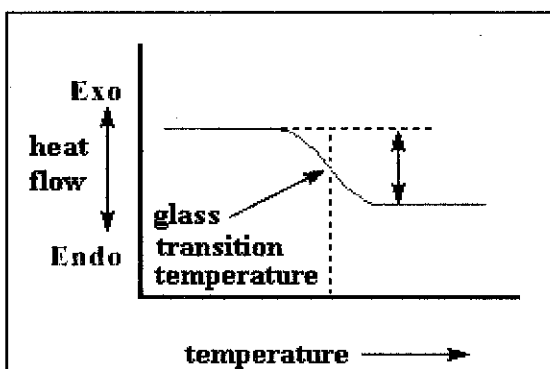


Figure 2.11: DSC Plot when polymer change state from glass to rubbery state

In DSC plot, glass transition temperature can be determined when the plot behave as in Figure 2.11. Tg is determine as middle of the incline state of the plot as shown in Figure 2.12

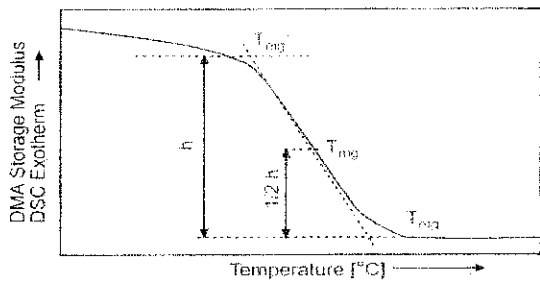


Fig. 5.7: Tangent constructions for the determination of the glass transition temperature as the "half height" from either DMA or DSC
 T_{onset} = extrapolated initial test temperature, onset temperature
 T_{mid} = middle point temperature
 T_{final} = extrapolated final temperature

Figure 2.12: Tangent construction for the determination of glass transition temperature

2.2.1.4 Crystallization

Above the glass transition, heat added to polymer makes them vibrate, rotate and eventually translate with limited space of molecular arrangement. This will continue until polymer gained enough energy to move into very ordered arrangements i.e. crystals.

When polymers fall into crystalline arrangement, heat will give off which indicates crystallization is an exothermic reaction. This can be observed in the plot of heat flow versus temperature.

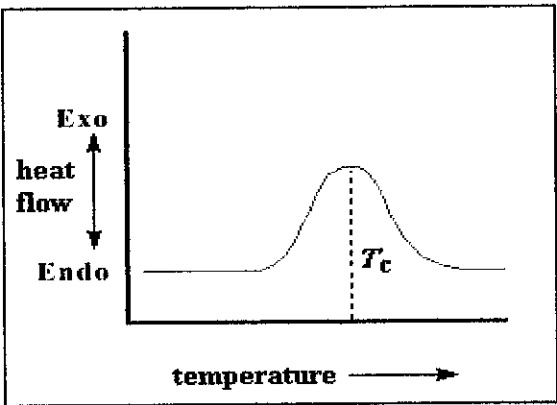


Figure 2.13: DSC plot at crystallization

There are many polymers' properties that can be observed from this peak. Temperature at highest point is polymer's crystallization temperature, T_c . Area of the peak give latent energy of crystallization for the polymer. However, more importantly, this peak tells the polymer can be crystallized. For example, if 100% amorphous polymer like atactic polystyrene is analyzed, the crystalline cannot be observed since the material does not crystallize. [12]

2.2.1.5 Melting

Heat may allow polymer to crystallize but excessive heat will make polymer crystal begin to fall apart and melt. This thermal transition is called melting. When the polymer crystals melt, heat is absorbed i.e. endothermic reaction. Melting is first order transition, which means, polymers' temperature won't rise until all the crystals have melted. This also means the furnace has to put additional heat into the polymer in order to melt both the crystals and keep the temperature rising at the same rate of reference pan. This extra heat flow during melting shows up as a large dip in our DSC plot as heat is absorbed by the polymer as shown in Figure 2.11 [12]

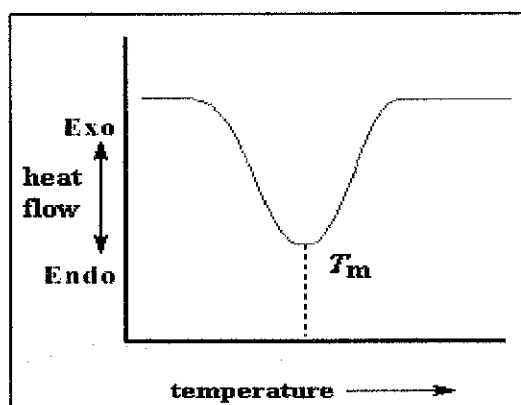


Figure 2.14: DSC Plot at melting

From DSC Plot, temperature at the apex of the dip is a melting point where the polymer is completely melted and heat of melting represents by area of this dip. [12]

2.2.1.6 Conclusion

Figure 2.12 represents full picture of DSC Plot from the beginning heat is supplied to the polymer.

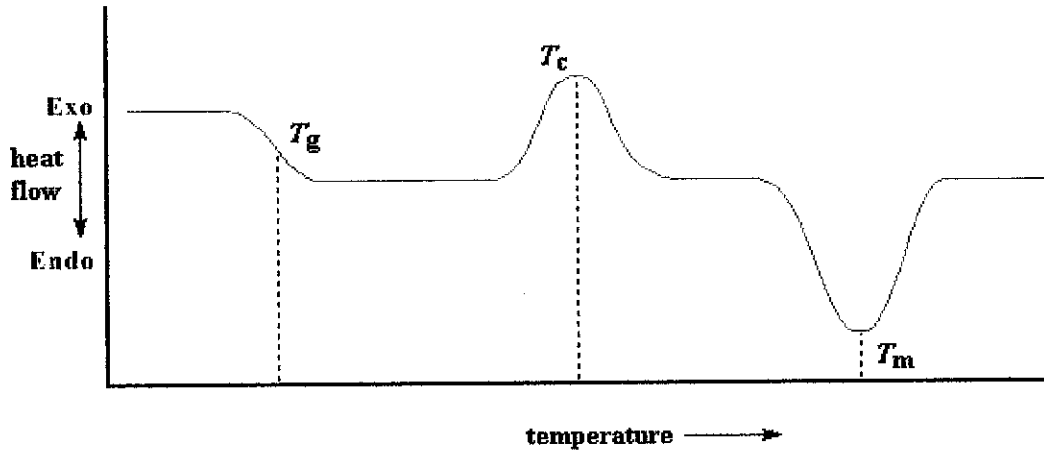


Figure 2.15: DSC Plot

It is important to notify that not all polymers will behave as such. The crystallization peak and the melting dip will only show up for polymers that can form crystals. Completely amorphous polymers won't show any crystallization, or any melting either. But polymers with both crystalline and amorphous domains will show all the features above.

There are big difference between the glass transition and the other two thermal transitions, crystallization and melting. For the glass transition, there is no peak, and there's no dip, either. This is because there is no latent heat given off, or absorbed, by the polymer during the glass transition. Both melting and crystallization involve absorbing or giving off heat. The only thing at the glass transition temperature is a change in the heat capacity of the polymer.

Because there is a change in heat capacity, but there is no latent heat involved with the glass transition, we call the glass transition a second order transition. Transitions like melting and crystallization, which do have latent heats, are called first order transitions. [12]

2.2.2 Dynamic Mechanical Analyzer

Dynamic Mechanical Analyzer (DMA) is an instrument designed for dynamic mechanical analysis. DMA measures the dynamic mechanical behaviour of samples as a function of temperature, e.g. the complex modulus of elasticity and the complex shear modulus.

In DMA, a sample is subjected to a sinusoidal mechanical deformation of frequency, f , and the corresponding force measured. Conversely, the sample can be subjected to defined force amplitude and the resulting deformation measured. [13]

2.2.2.1 DMA Plot

During deformation measurement of samples, DMA will give a plot of its analyze plot. Three important analyze plot are Young or Elastic Modulus, Loss Modulus, and Tangent Delta.

2.2.2.2 Young Modulus

The Young Modulus or storage modulus, M' is defined as the amount at which a material stretches or deforms when a force or stress is applied [14]. A material with a high modulus of elasticity experiences very little stretching, even for high forces. The storage modulus is also defined as slope of the stress-strain curve (Figure 2.16) in the elastic region. This relationship is Hooke's Law: $E = \frac{\sigma}{\epsilon}$

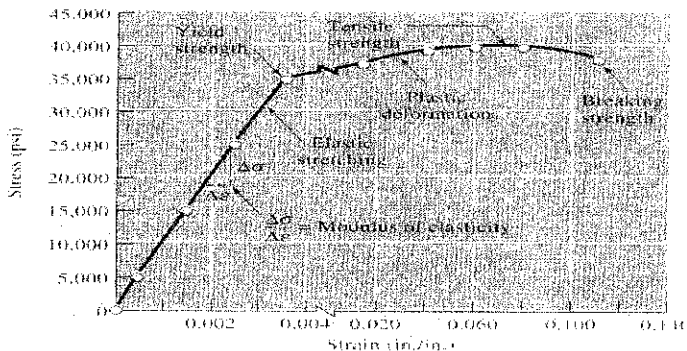


Figure 2.16: The stress-strain curve for an aluminium alloy

The storage modulus is closely related to the binding energies (Figure 2.17). A steep slope in force-distance graph at the equilibrium spacing indicates that high forces are required to separate the atoms and cause the material to stretch elastically.

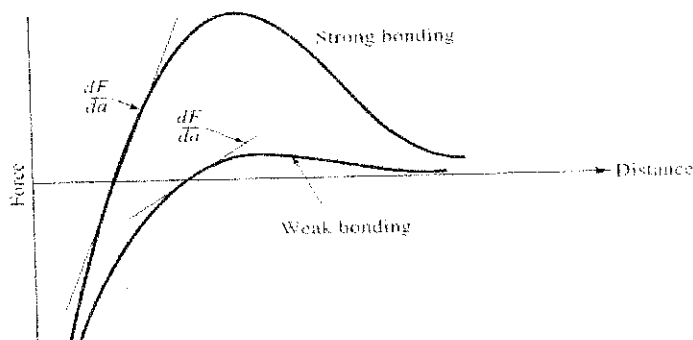


Figure 2.17: The force-distance curve for two materials

The modulus is a measure of stiffness of the material. A stiff material, with a high modulus of elasticity, maintains its size and shape even under an elastic load. [14]

2.2.2.3 Loss Modulus

Loss Modulus, M'' can be related to the work dissipated within the material during one load cycle. It indicates, for example, the energy converted into heat and can hence be used as a measurement of the viscous component, or unrecoverable oscillation dissipated per cycle. [11]

2.2.2.4 Tangent Delta

The phase angle δ indicates the phase shift between the stress and the strain signal. The tangent of the phase angle, known as the loss tangent \tan , is used to define the relationship between the loss and storage moduli. This is usually used to measure the energy loss in relation to the recoverable energy and is therefore dimensionless. It can also be used to indicate the mechanical absorption or internal friction of a viscoelastic system. A high $\tan \delta$ value signifies a material that will demonstrate highly inelastic deformation behaviour. A lower value characterizes a material that will behave more elastically and only purely elastic material can achieve a value of 0. [11]

A schematic representation of storage modulus, loss modulus and tangent delta are represents in Figure 2.18

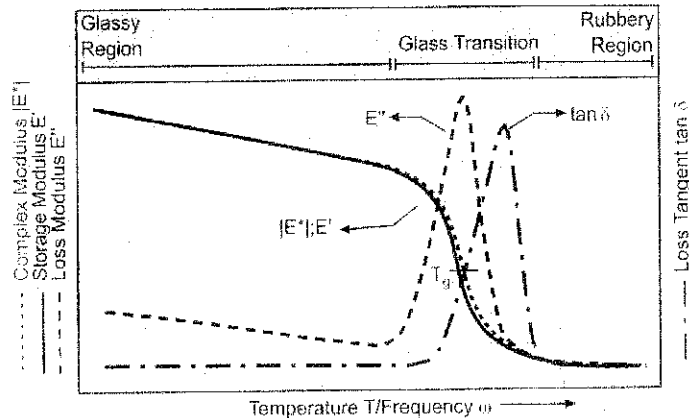


Figure 2.18: Complex modulus $|E^*|$, storage modulus E'' , loss modulus E'' and loss tangent $\tan \delta$

2.2.3 High Pressure Liquid Chromatography

2.2.3.1 Chromatography

Chromatography is an analytical chemical process for the separation of mixtures involving passing a sample (the analyte) in the "mobile phase", often in a stream of solvent, through the "stationary phase", some form of material that will provide resistance by virtue of chemical interactions (not reactions) between the components of the sample and the material. Usually, each component has a characteristic separation rate that can be used to identify it and thus the composition of the original mixture.

A chromatograph takes a chemical mixture carried by liquid or gas and separates it into its component parts as a result of differential distributions of the solutes as they flow around or over a stationary liquid or solid phase. Various techniques for the separation of complex mixtures rely on the differential affinities of substances for a gas or liquid mobile medium and for a stationary adsorbing medium through which they pass; such as paper, gelatin, or magnesium silicate gel.

Analytical chromatography is used to determine which chemicals are in a mixture and their concentrations. Preparative chromatography is used to purify larger

quantities of a chemical. Most of the following refers to analytical chromatography. [15]

2.2.3.2 High Pressure Liquid Chromatography



Figure 2.19: High Pressure Liquid Chromatography

Frequently referred to simply as HPLC, this form of column chromatography is used frequently in biochemistry. The analyte is forced through a column by liquid at high pressure, which decreases the time the separated components remain on the stationary phase and thus the time they have to spread out within the column, leading to broader peaks.

Less time on the column then translates to narrower peaks in the resulting chromatogram and thence to better selectivity (it's easier to differentiate one peak from another) and sensitivity (tall, narrow peaks can be easier to discriminate from noise than shorter, broader peaks). Solvents used include any miscible combination of water or various organic liquids (alcohols, acetonitrile, dichloromethane). Often, a gradient over time in the solvent composition passing through the column is used to separate analyte mixtures, as a function of how well the changing solvent composition differentially mobilizes the analyte. For instance, using a water/methanol gradient, the more hydrophobic components will elute under conditions of relatively high methanol, whereas the more hydrophilic will elute under conditions of relatively low methanol. Whether one starts with high methanol or low methanol depends on the nature of the stationary phase. [16]

2.2.3.3 Reversed phase liquid chromatography

Traditionally HPLC stationary phases are polar, whereas so-called "reverse" phase (RP-HPLC) stationary phases are hydrophobic. On an RP-HPLC column, then, hydrophobic analytes would tend to be retained on the column, eluting more readily as the proportion of the hydrophobic component of the stationary phase is increased. RC-HPLC has lower resolution than GC. [16]

CHAPTER 3

METHODOLOGY

3.1 ELEMENTS DETERMINATION

This research project work can be divided into two major section, which are:

- (I) Sample Preparation
- (II) Sample Characterization and Comparison

Sample preparation is process of synthesizing surfactant from fatty acids. Consequently, sample characterization and comparison is a process of characterization properties of synthesize and commercial surfactant for comparison purposes. This comparison in characteristic is done to enhance surfactant from fatty acids properties so that it attests to industrial application of oil and gas industry.

3.2 SAMPLE PREPARATION

Two major processes are involved in synthesis of surfactant from fatty acid. They are:

3. Purification process
4. Saponification process

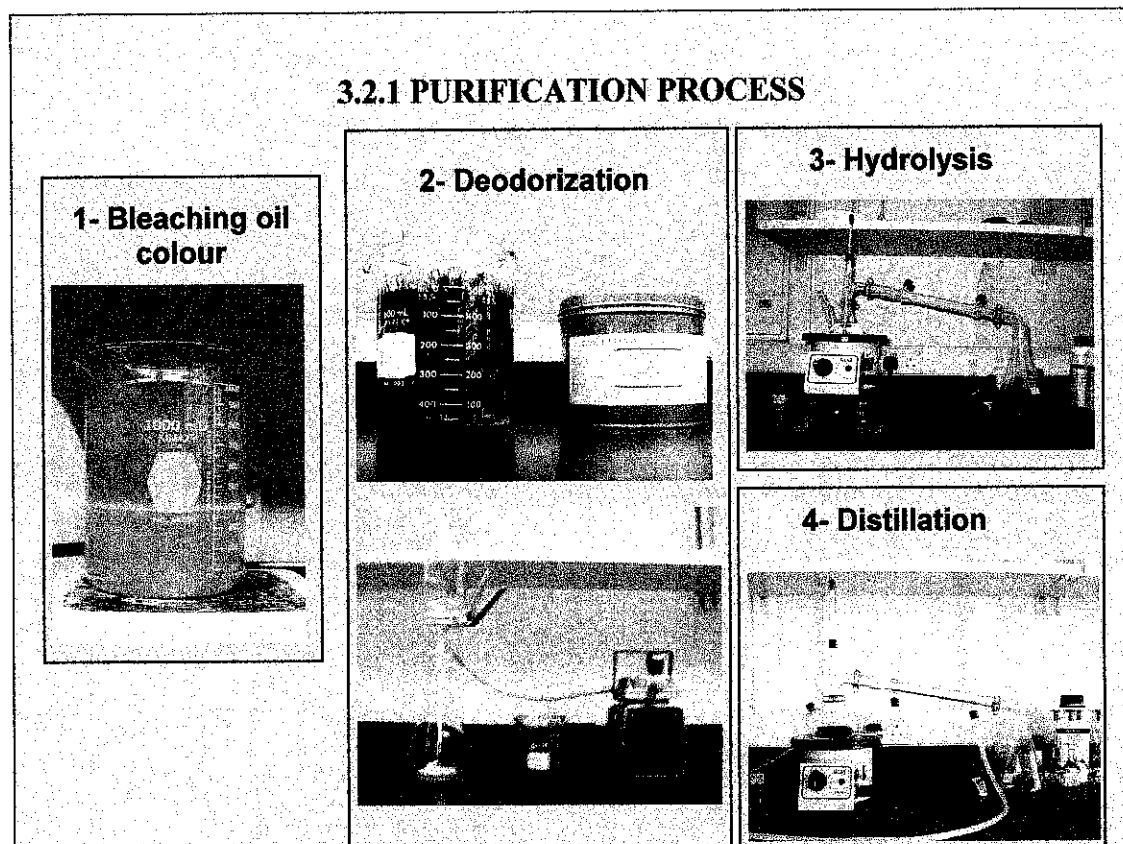
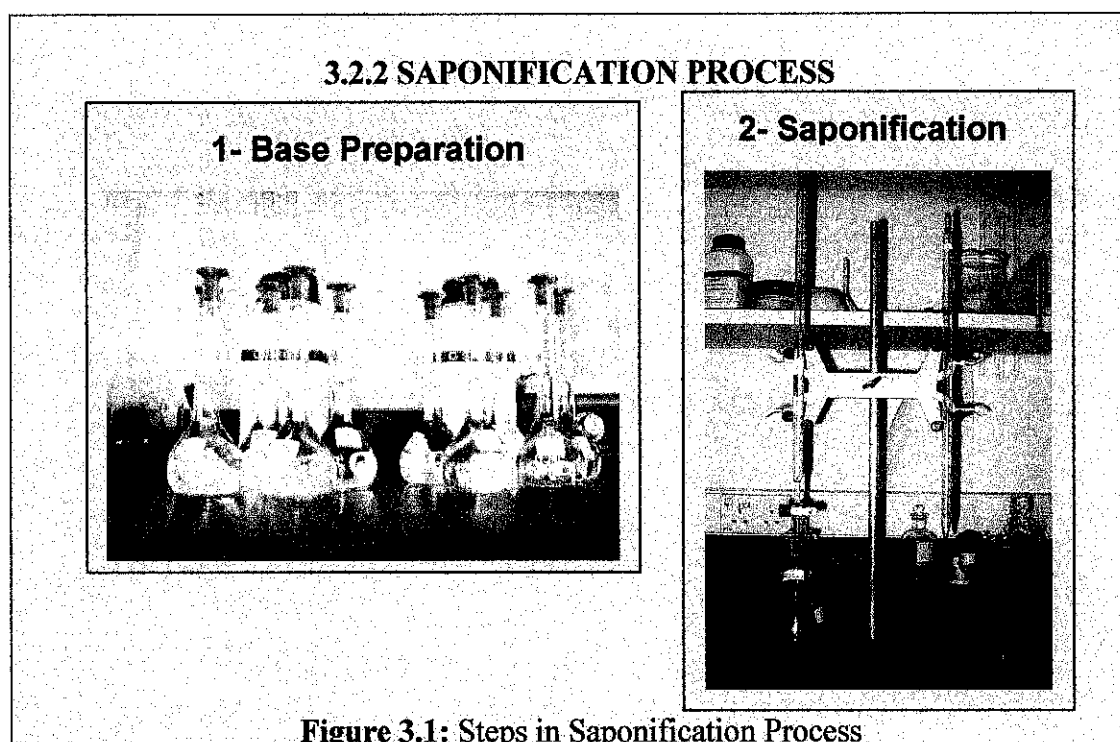


Figure 3.0: Steps in Purification Process

ACTION	OBSERVATION
<p>(I) Bleached Oil Colour Palm Oil is heated to 70°C. Hydrogen peroxide is added slowly to the under air agitation for one hour. The mixing palm oil and hydrogen peroxide is stir until three hours.</p>	<p>Palm Oil colour is reduced but does not reduce completely. Layers created between oil and hydrogen peroxide.</p>
<p>Palm Oil that has been mixed with hydrogen peroxide is separated manually. The hydrogen peroxide is considered as a waste.</p>	<p>Some of palm oil cannot be gained during this manually separated and some hydrogen peroxide goes into the palm oil collected during manually separated process.</p>
<p>(II) Deodorization The 'bleached' oil is mixed with activated carbon to deodorize the oil.</p>	<p>Oil is black in colour due to mixing with activated carbon. Oil odour cannot be traced anymore but hydrogen peroxide odour still exists in the oil.</p>

<p>The odourless oil is then filtered by aid of pump.</p>	<p>The oil colour is slightly clearer than oil after bleaching process.</p>
<p>(III) Hydrolysis Process By aid of set up hydrolysis apparatus, water is boiled continuously to its boiling point. Steam from boiling water is supplied into odourless oil which makes reaction between continuous steam and oil (hydrolysis)</p> <p>(IV) Distillation of fatty acid from oil contaminants The yellow layer which identified as ester (fatty acid) and water layer which identified as alcohol is boiled to 70-80°C which is alcohol boiling point temperature. The boiled alcohol is condensed by aid of water and droplet of alcohol form and collected at end of condenser system. The fatty acid can be collected once all of alcohol form has been condensed as end product. Temperature control of boiled solution must be maintained and taken care during this experiment.</p>	<p>Two layers of oil can be observed from hydrolysis reaction. The upper layer is yellow in colour while the second layer is water in colour. Colour of oil is slightly clearer. No odour changes detected.</p> <p>The oil fatty acid colour turns pale in colour. The product is keep for saponification process.</p>



ACTION	RESULTS																		
<p>(I) Preparation of NaOH and KOH</p> <p>0.1M, 0.25M, 0.225M, 0.275M and 0.3M of NaOH and KOH is prepared using volumetric flask 100ml. Mass of each molarity is calculate using :</p> <div><p>Mass= molarity x volume x MW</p></div>	<p>Mass calculated from each molarity:</p> <table><tr><th>Molarity</th><th>NaOH (MW= 40)</th><th>KOH (MW= 56.11)</th></tr><tr><td>0.1M</td><td>0.4g</td><td>0.5611g</td></tr><tr><td>0.2M</td><td>0.8g</td><td>1.1222g</td></tr><tr><td>0.225M</td><td>0.9g</td><td>1.2625g</td></tr><tr><td>0.275M</td><td>1.1g</td><td>1.5430g</td></tr><tr><td>0.3M</td><td>1.2g</td><td>1.6833g</td></tr></table>	Molarity	NaOH (MW= 40)	KOH (MW= 56.11)	0.1M	0.4g	0.5611g	0.2M	0.8g	1.1222g	0.225M	0.9g	1.2625g	0.275M	1.1g	1.5430g	0.3M	1.2g	1.6833g
Molarity	NaOH (MW= 40)	KOH (MW= 56.11)																	
0.1M	0.4g	0.5611g																	
0.2M	0.8g	1.1222g																	
0.225M	0.9g	1.2625g																	
0.275M	1.1g	1.5430g																	
0.3M	1.2g	1.6833g																	
<p>(II) Titration Of NaOH/KOH With Purified Oil</p> <p>Phenophtalein is used as indicator in this titration to achieve surfactant of pH7 (neutral).</p>	<p>When fatty acid (purified oil) change to pink in colour, volume of NaOH/KOH is recorded.</p> <table><tr><th></th><th>NaOH (pH≈7)</th><th>KOH (pH≈7)</th></tr><tr><td>0.1M</td><td>0.92ml</td><td>1.62ml</td></tr><tr><td>0.2M</td><td>0.85ml</td><td>1.20ml</td></tr><tr><td>0.225M</td><td>0.75ml</td><td>1.13ml</td></tr><tr><td>0.275M</td><td>0.63ml</td><td>0.86ml</td></tr><tr><td>0.3M</td><td>0.48ml</td><td>0.63ml</td></tr></table>		NaOH (pH≈7)	KOH (pH≈7)	0.1M	0.92ml	1.62ml	0.2M	0.85ml	1.20ml	0.225M	0.75ml	1.13ml	0.275M	0.63ml	0.86ml	0.3M	0.48ml	0.63ml
	NaOH (pH≈7)	KOH (pH≈7)																	
0.1M	0.92ml	1.62ml																	
0.2M	0.85ml	1.20ml																	
0.225M	0.75ml	1.13ml																	
0.275M	0.63ml	0.86ml																	
0.3M	0.48ml	0.63ml																	
<p>Titration processes is repeated by volume acquired.</p>	<p>The form surfactant is keep in 10 plastic bottles of various molarity.</p>																		

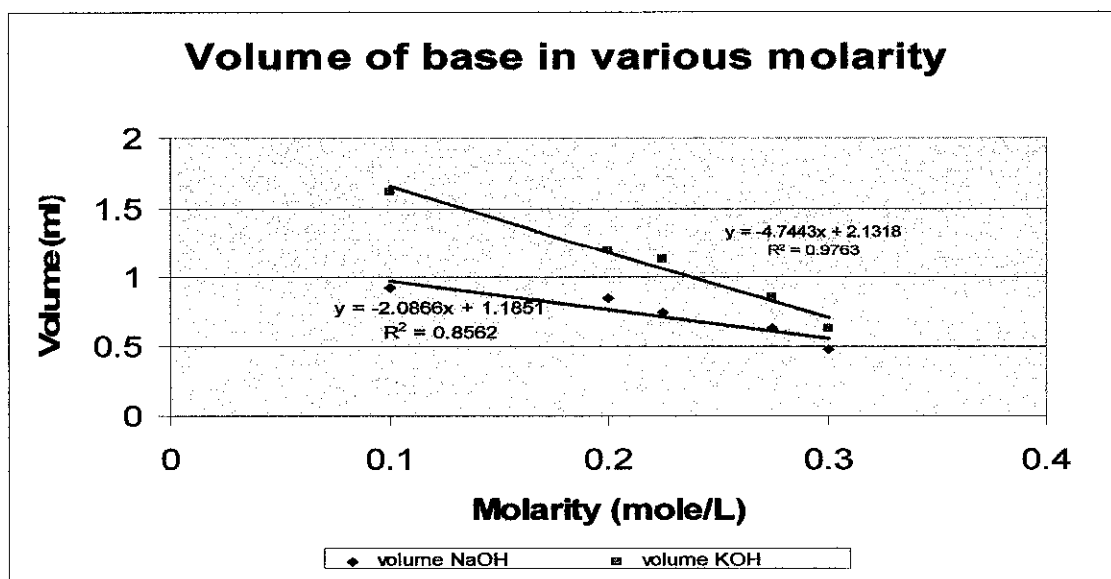


Figure 3.2: Volume of base titrate for various molarity

3.3 SAMPLE CHARACTERIZATION AND COMPARISON

3.3.1 Conductivity Test

STEP	ACTION
1	Sample is transfer into test tube
2	Electrode is put into sample and conductance meter will give reading of conductivity in $\mu\text{S}/\text{cm}$.
3	Record conductivity reading
4	Plot graph conductivity measured vs. various molarity for synthesize samples

3.3.2 Surfactants' Effectiveness Test

STEP	ACTION	REMARKS
1	Sample of synthesis surfactant and commercial surfactant is mixed with crude oil	
2	Shake and observe its miscibility	Both were miscible
3	Titrate brine to synthesize surfactant until two layers observe	Synthesize surfactant used = 0.2M NaOH base surfactant
4	Record brine volume	
5	Repeat step 3 to 4 to commercial surfactant	Commercial surfactant used = 0.2M

3.3.3 Differential Scanning Calorimeter (DSC)

STEP	ACTION	REMARKS
1	Supply nitrogen to DSC.	
2	Weigh synthesize surfactant	Synthesize used = 0.2M NaOH Weight _{s,s} = 7.1mg
3	Punch the synthesize surfactant and empty aluminium sample pan and insert them into the pan holder of DSC.	Empty aluminium sample pan is used as DSC reference

4	Temperature range is set from 10°C – 400°C while temperature rate is set to 10°C/min	
5	Start graph recorder when DSC temperature achieves 10°C.	
6	Print out recorded graph when temperature ends at 400°C	
7	Repeat experiment from Step 2 to Step 6 for commercial surfactant.	Commercial Surfactant = 0.2M Weight _{c.s} =7.3mg

3.3.4 Dynamic Mechanical Analyzer (DMA)

STEP	ACTION	REMARKS
1	Supply liquid nitrogen to DMA	
2	Mount two O-rings between the disk of shear clamp	
3	Fill the syringe with synthesize surfactant	Synthesize used = 0.2M NaOH
4	Inject the side of the O-ring with synthesize surfactant until it penetrates through the first hole. Repeat for second hole.	
5	Cool the furnace insulation to 10°C	
6	Measure diameter and thickness of the O-ring using vernier clipper. Insert the values to DMA installation windows	
7	Temperature range is set from 10°C – 250°C while temperature rate is set to 10°C/min	
8	Start graph recorder when DMA temperature achieves 10°C	
9	Print out recorded graph when temperature ends at 250°C	
10	Repeat experiment from Step 3 to Step 9 for commercial surfactant.	Commercial Surfactant = 0.2M

3.4 APPARATUS REQUIRED

3.4.1 Sample Preparation

No	Process	Apparatus	Chemical's required
3.4.1.1 Purification Process			
1	Bleaching Oil Colour	Weight balance, beaker, heater, thermometer, stirrer	Palm Oil, Hydrogen Peroxide 30%
2	Deodorization	Beaker, TSS Apparatus, Pump	Bleached Oil, Activated Carbon
3	Hydrolysis Process	Round Bottom Flask, Distillation Set, Thermal Heater, Thermometer, Silicon Tube, Conical Flask	Odourless Oil, Distilled Water
4	Distillation of ester from oil contaminants	Round Bottom Flask, Distillation Set, Thermal Heater, Thermometer, Conical Flask	Hydrolysed Oil
3.4.1.2 Saponification Process			
1	Base Preparation	Weight balance, Volumetric Flask	Sodium Hydroxide, Potassium Hydroxide, Water
2	Titration	Burette, Conical Flask, Volumetric Cylinder, Phenolphthalein	Purified Oil, Base prepared

3.4.2 Sample Characterization and Comparison

No	Process	Apparatus	Chemical's required
3.4.2.1 Conductivity Test			
1	Conductivity Test	Conductance Meter, Beaker, Distilled Water	Synthesize Surfactant, Commercial Surfactant
3.4.1.2 Surfactants' Effectiveness Test			
1	Sample Preparation	Test Tube, Stopper	Crude Oil, Synthesize and Commercial Surfactant
2	Surfactants' Effectiveness Test	Burette, Conical Flask, Volumetric Cylinder,	Sample Prepared, Brine Water
3.4.1.3 Differential Scanning Calorimeter (DSC)			
1		Differential Scanning Calorimeter (DSC)	Gas Nitrogen, Synthesize Surfactant, Commercial Surfactant
3.4.1.4 Dynamic Mechanical Analyzer (DMA)			
1		Dynamic Mechanical Analyzer (DMA)	Liquid Nitrogen, Synthesize Surfactant, Commercial Surfactant

CHAPTER 4
RESULTS AND DISCUSSION

4.1 RESULTS

4.1.1 Conductivity Test

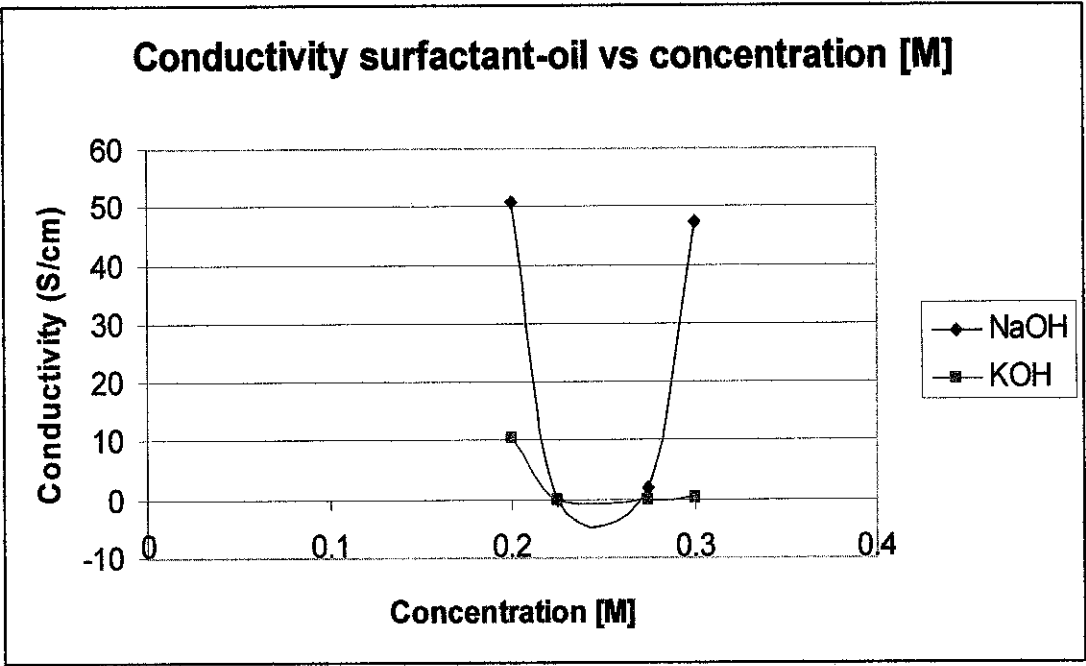


Figure 4.0: Result of Conductivity Test Experiments

4.1.2 Surfactants' Effectiveness Test

Table 4.0: Results of Surfactants' Effectiveness Experiment

Synthesize Surfactant	Commercial Surfactant
49.8 ml of water	17 ml of water

4.1.3 Differential Scanning Calorimeter (DSC)

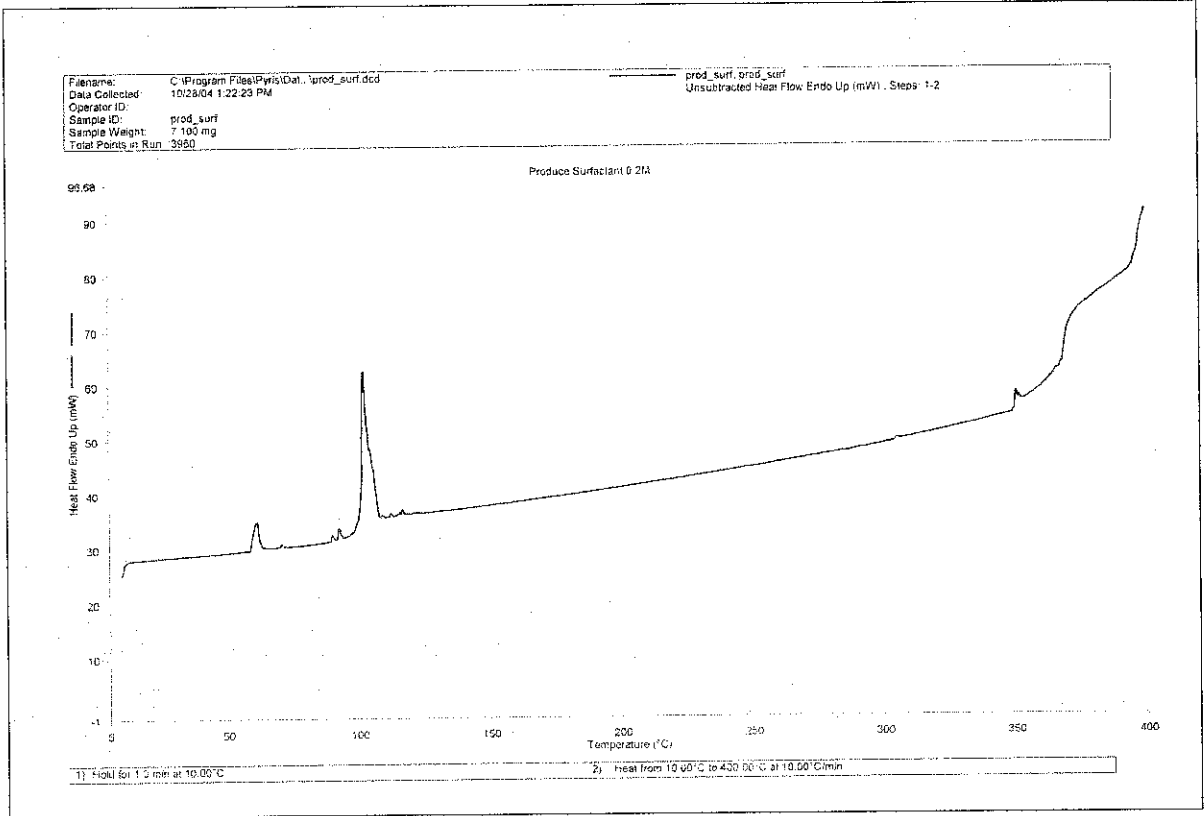


Figure 4.1: DSC Experimental Results for Synthesize Surfactant

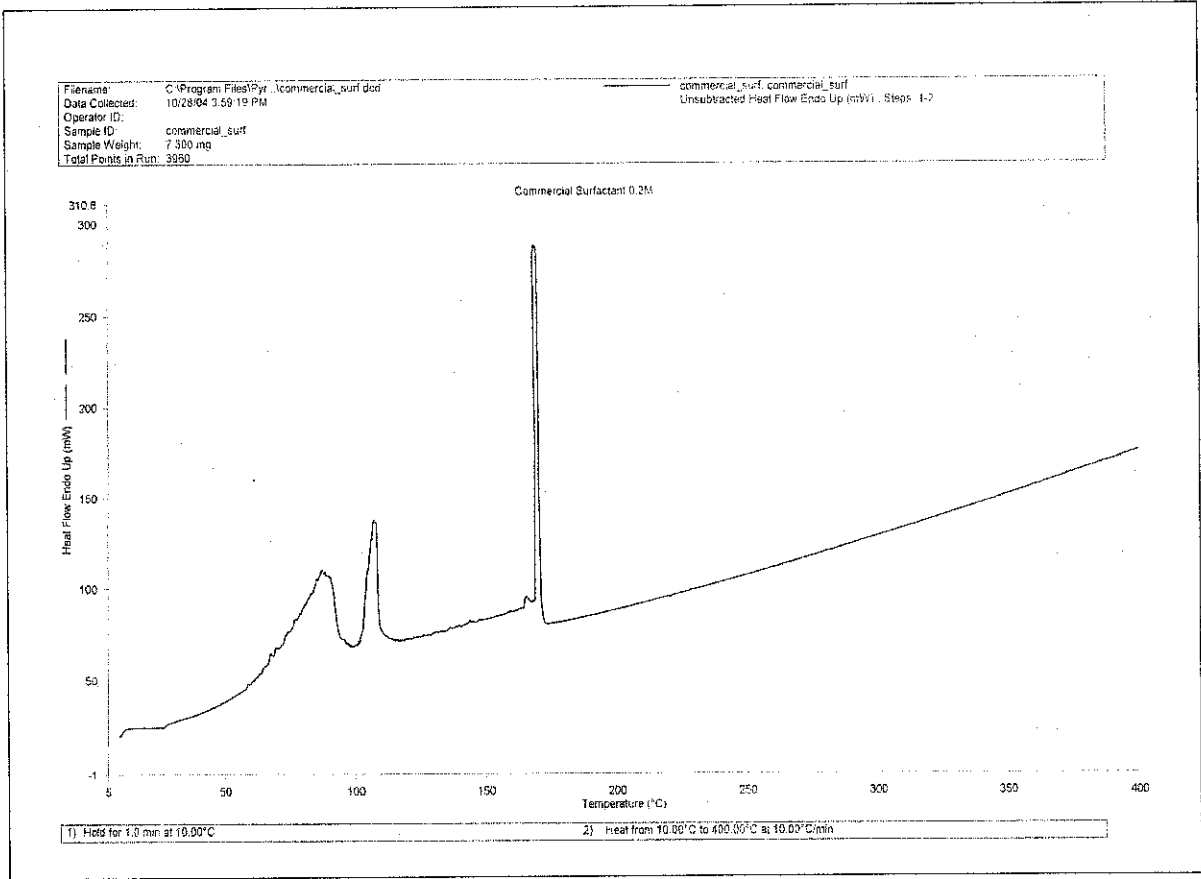


Figure 4.2: DSC Experimental Results for Commercial Surfactant

4.1.4 Dynamic Mechanical Analyzer (DMA)

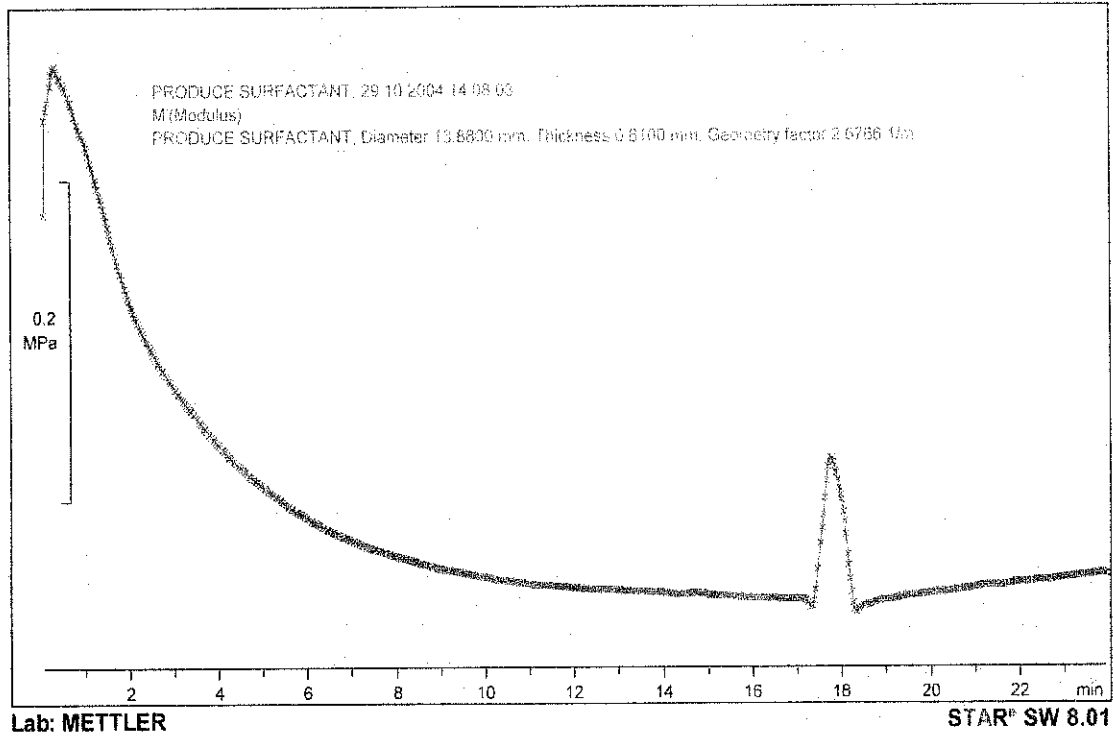


Figure 4.3: DMA Young Modulus, M' Experimental Results for Synthesize Surfactant

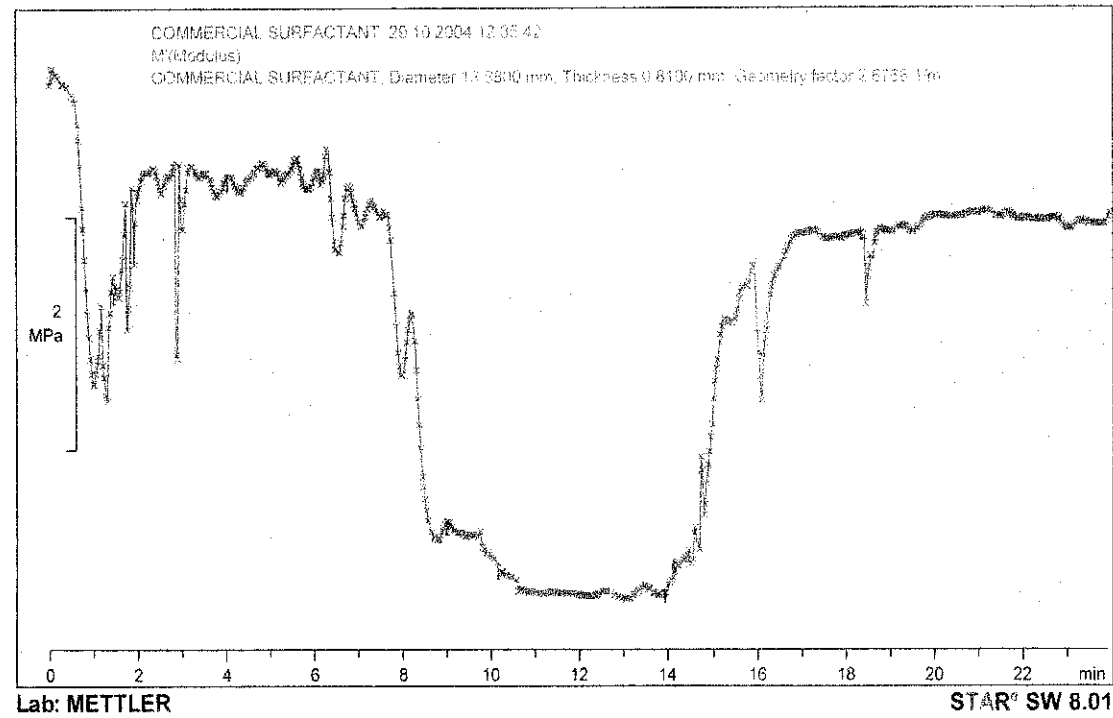


Figure 4.4: DMA Young Modulus, M' Experimental Results for Commercial Surfactant

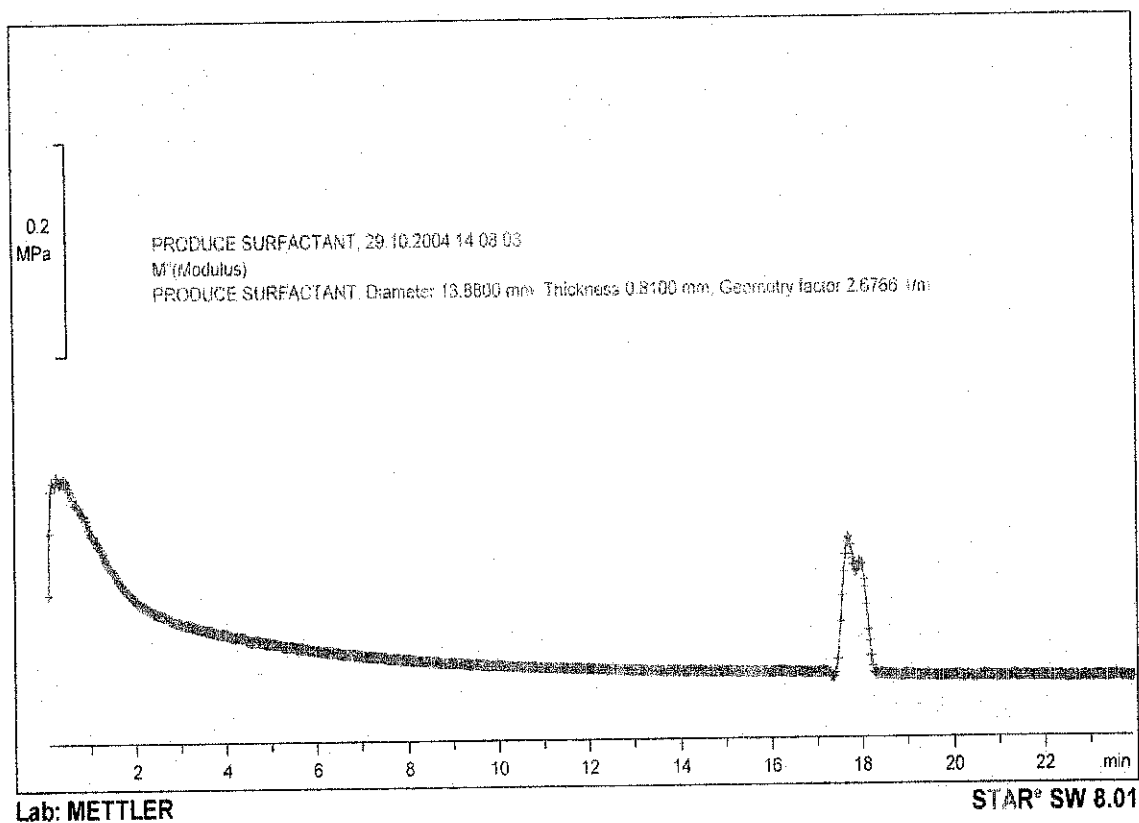


Figure 4.5: DMA Loss Modulus, M'' Experimental Results for Synthesize Surfactant

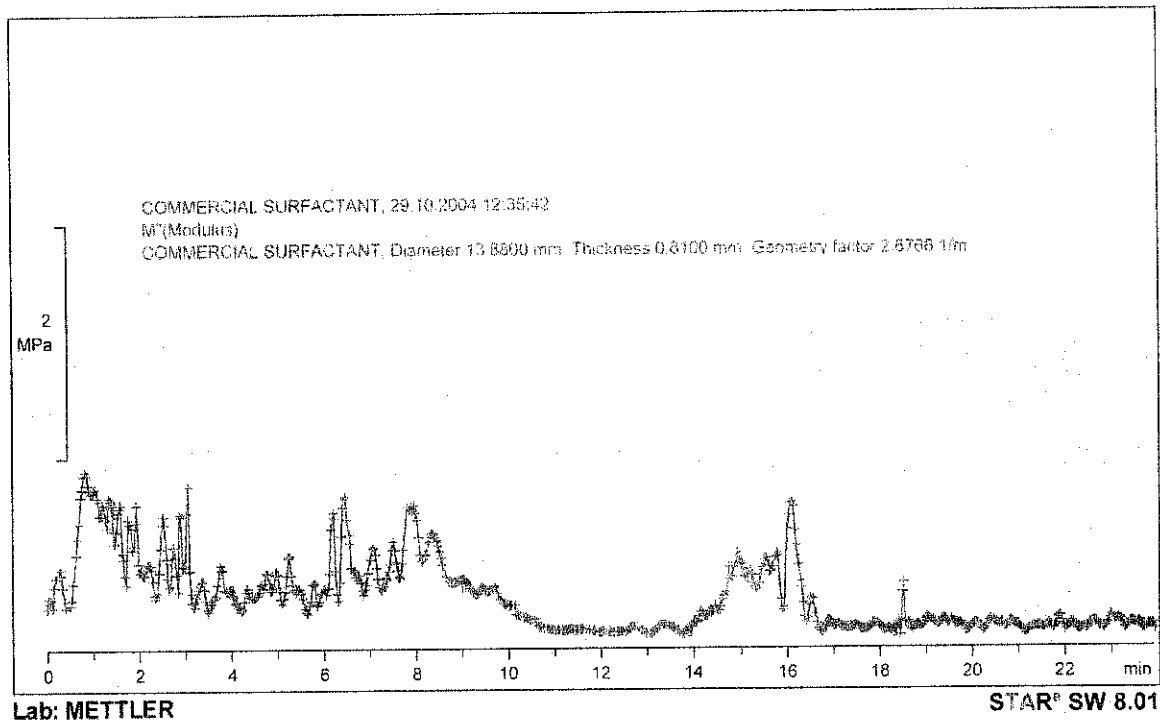


Figure 4.6: DMA Loss Modulus, M'' Experimental Results for Commercial Surfactant

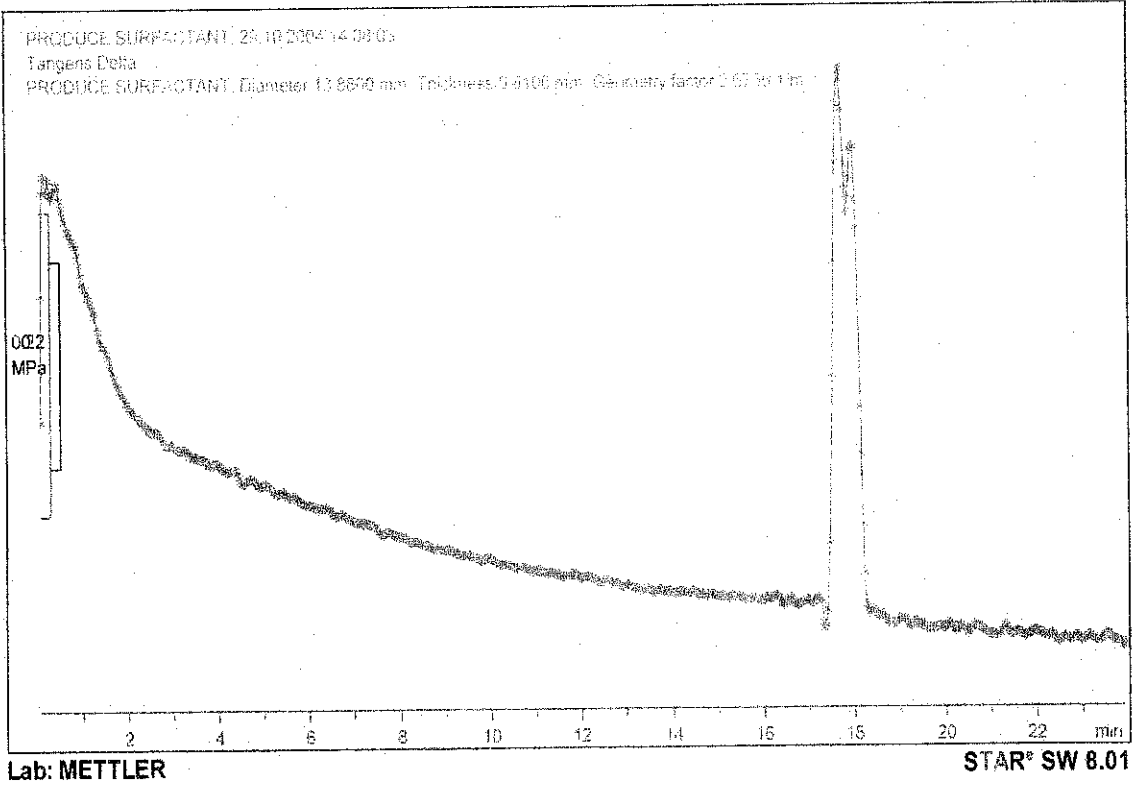


Figure 4.7: DMA Tangents Delta, $\tan \delta$ Experimental Results for Synthesize Surfactant

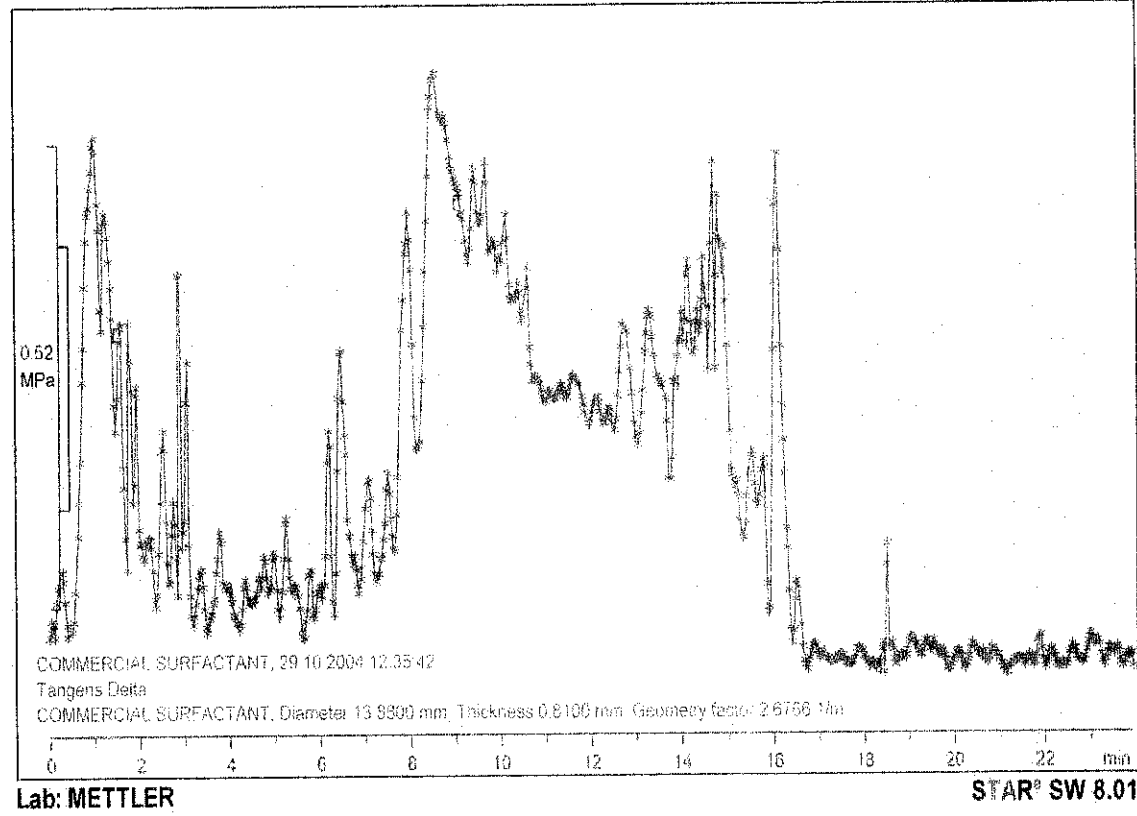


Figure 4.8: DMA Tangents Delta, $\tan \delta$ Experimental Results for Commercial Surfactant

4.2 DISCUSSION

4.2.1 Conductivity Test

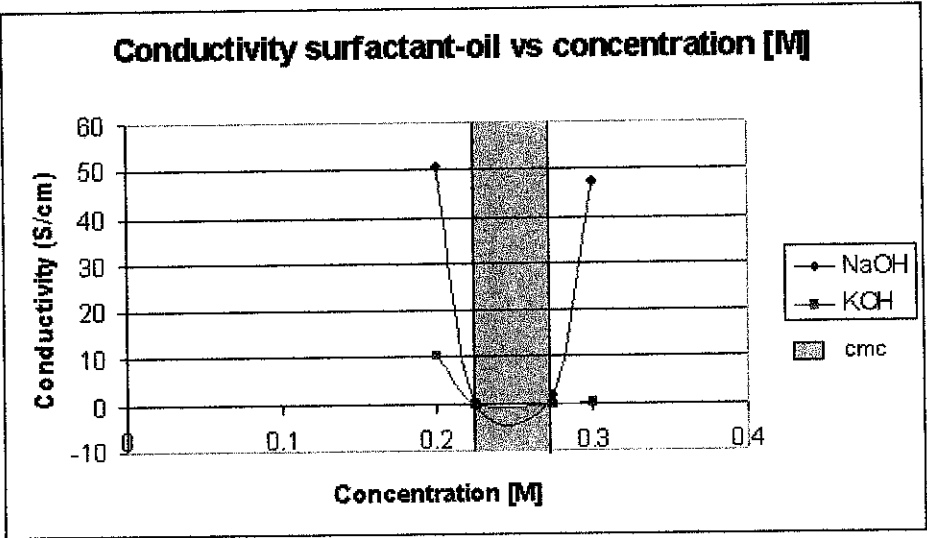


Figure 4.9: Result of Conductivity Test Experiments

CONDUCTIVITY PHASES	ORGANISATION OF MICELLES	PHASE DIAGRAM AND COMPOSITION
BEFORE CMC		
DURING CMC		
AFTER CMC		

Discussion:

The importance of conductivity inside the oil-surfactant emulsions: The conductivity of material is determined by the electronic structure of the atoms. Conductivity of materials can be change by influencing the mobility, μ , of the carriers. The mobility is proportional to the drift velocity, \bar{v} , which is low if the electrons collide with imperfections in the lattice [14]. In the reservoir, oil which is isolated structure of rock is immobilize because drift velocity has collide with imperfection of the rock lattice. Thus, surfactant in oil-surfactant injection is important to act as a material which influences the mobility of oil. The mean free path is the average distance between collisions; a long mean free path permits high mobilities and high conductivities [14] Since surfactant have properties of low interfacial tension, it is predicted to be one of best mobile for oil conductivity. However, surfactant has properties of micelle concentration, which in certain concentration cannot govern oil in emulsion form. Thus, we have to understand oil-surfactant behaviour in micelle concentration.

Conductivity below CMC- In this region, conductivity between continuously decreases. Thus, provide low mobile ability to the oil-surfactant form. Besides at this point, oil-surfactant cannot fully in contact to each other due to low micelle concentration. In this region, oil-surfactant emulsion does not form due to low micelle concentration. That's why, at this phase, no oil swelling has taken place in this region and it's is classified as Phase II of Surface Phase Behaviour.

Conductivity at CMC- In this region, conductivity is still decreasing even oil-surfactant emulsion have been form. The form emulsion explains why bottom aqueous phase is coloured. Conductivity is low during critical micelle concentration can be explain by brine content in reservoir which dissolve in surfactant. This also explains why phase behaviour at cmc is classified as Phase II- of Surface Phase Behaviour.

Conductivity above CMC- CMC achieve when high concentration of sodium apply to surfactants. In this region, adsorption of surfactants onto reservoir surfaces increases very little. However, this condition is contrast to adsorption of oil into

surfactant. Above cmc is the best condition where adsorption of oil-surfactant emulsified. This explains why conductivity starts to increase. In this region, high salinity does not affect phase behaviour of oil-surfactant unless condition of too high salinity occurred. In this region, all surfactant/volume capable to emulsify is in contact with oil. These makes it as most desired phase behaviour target in chemical flooding. This is because, Phase III envelope minimize surfactant losses, thus provide economic feasibility to investor of oil field.

NaOH vs. KOH- From graph plotted, conductivity of potassium does not increase much even after critical micelle concentration. This explains why commercial surfactants are sodium base and not potassium base.

4.2.2 Surfactants' Effectiveness Test

Surfactant's effectiveness test is done to compare the effectiveness between synthesize and commercial surfactants. This is done by simple titration of brine water to oil-surfactants emulsion. The two layers form by titration indicates the end point of surfactants effectiveness. From comparisons, it can be conclude that synthesize surfactants have higher effectiveness than commercial surfactants by ratio 3:1.

4.2.3 Differential Scanning Calorimeter (DSC)

NO	ELEMENTS	COMPARISON OF SURFACTANTS	
		Synthesize	Commercial
1	Peak	Two Peak at 60°C and 110°C	Three Peak at 80°C, 110°C and 170°C

Discussion:

The same baseline with almost equivalent first and second peak indicates both synthesis and commercial surfactants have same molecular agitecture. The third peak of commercial surfactant indicates there are additives inside commercial surfactant. The additives in this commercial surfactant make it experienced three transition phase changes or in other words provides it with untangle structure after a second deformation.

2	Specific heat capacity	<ul style="list-style-type: none"> Heat flow at first peak= $35\text{mW}=35\text{mJ/min}$ Heating flow rate = 10°C/min Sample weight = 7.1mg $C_p=(35\text{mJ/min})(1/10^{\circ}\text{C/min})$ $(1/7.1\text{mg}) = \mathbf{0.4930\text{ J/g}^{\circ}\text{C}}$ 	<ul style="list-style-type: none"> Heat flow at first peak= $110\text{mW}=110\text{mJ/min}$ Heating flow rate = 10°C/min Sample weight = 7.3mg $C_p=(110\text{mJ/min})(1/10^{\circ}\text{C/min})$ $(1/7.3\text{mg}) = \mathbf{1.5068\text{ J/g}^{\circ}\text{C}}$
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Discussion:

Specific heat capacity, C_p is defined as the heat required to raise unit mass of substance by one degree of temperature. Since DSC Plot is Heat flow vs. Temperature, The C_p can be calculated from the first phase transition as calculated above. From equation $Q=mC_pdT$, higher C_p indicates the materials have higher ability to absorb heat. Thus, by calculation above, commercial surfactant have higher ability to absorb heat.

3	Endothermic reaction	Peak above the trendline indicates the material absorb heat	Peak above the trendline indicates the material absorb heat
---	----------------------	-------------------------------------------------------------	-------------------------------------------------------------

Discussion:

Both synthesize and commercial surfactant does not experience Glass Transition Temperature, Crystallization or Melting. However, DSC Plot indicates these materials continuously absorb heat during phase transition. This indicates these materials experience endothermic reaction each time they experience phase transition.

4.2.4 Dynamic Mechanical Analyzer (DMA)

NO	ELEMENTS	COMPARISON OF SURFACTANTS	
		Synthesize	Commercial
1	Young Modulus, M'	<ul style="list-style-type: none"> A plot with only one peak oscillation A stretch above 0.2MPa with a peak $\approx 17.5\text{ min}$ 	<ul style="list-style-type: none"> A plot with too many oscillations. A stretch above 2MPa with obvious valley between $\approx 8\text{-}14.9\text{min}$ with a peak at $\approx 16.8\text{min}$

Discussion:

The Young Modulus or storage modulus, M' is defined as the amount at which a material stretches or deforms when a force or stress is applied. From DMA Plot, synthesize surfactant have very little stretching compared to commercial surfactant.

This indicates synthesized surfactant have higher storage modulus, and stiffer material compare to commercial surfactant. Stiffer materials means it have regulated and ordered molecular structure i.e. have higher binding energies [14]

A plot with only one peak oscillation in synthesized surfactant indicates it as solid-liquid phase material while a plot with many peak oscillation in commercial surfactant indicates it as a total liquid phase materials.

The approximate peak at 17.5min and 16.8min in synthesized and commercial surfactant respectively signifies there are same material inside both of them which have same component and same molecular agitecture.

2	Loss Modulus, M''	A stretch below 0.2MPa with a peak ≈ 17.5 min	A stretch below 2MPa with obvious valley between ≈ 8 -14.9min with a peak at ≈ 16.8 min
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Discussion:

Loss Modulus, M'' can be related to the work dissipated within the material during one load cycle. Rate of material displacement to recover from its stretching condition to original phase indicates loss modulus. This explains why loss modulus value is small compare to Young Modulus. The rate of material displacement is also a measurement of material viscosity. From DMA Plot, synthesized surfactant recover faster to its original position than commercial surfactant. Consequently, synthesized surfactant is a more viscous fluid than commercial surfactant.

3	Tangent Delta, $\tan \delta$	$\tan \delta = 0.2$	$\tan \delta = 0.5$
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Discussion:

The tangent of the phase angle, known as the loss tangent $\tan \delta$, is used to define the relationship between the loss and storage moduli, i.e. $\tan \delta = M''/M'$. Thus synthesized surfactant, have lower $\tan \delta$, which means it behave more elastically and have lower mechanical absorption than commercial surfactant.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

- 1) Conductivity is important properties since it favour mobility of emulsion in reservoir.
- 2) Higher conductivity at above critical micelle concentration region is the best condition to get emulsion in three phase behaviour.
- 3) Potassium based surfactant does not represents favourable behaviour to enhance oil recovery.
- 4) Surfactants effectiveness test shows synthesize surfactants to have higher ability to sustain oil under brine flooding condition.
- 5) Synthesize surfactants have almost similar molecular agitecture to commercial surfactant.
- 6) Synthesize surfactant should be improved by means of adding its transition, and lowering its modulus/viscosity.
- 7) Additive is predicted to be one of commercial surfactant component which favour its third phase transition, lowering its modulus/viscosity/interfacial tension.

5.2 RECOMMENDATION

This recommendation is done with hope this research will continually done so that this idea can be enhance and attest in future industrial application.

- 1) It is recommended High Pressure Liquid Chromatography (HPLC) can be done to this experiment. This is because HPLC can determine chemical compound in synthesis surfactant, permit comparison between synthesize and commercial surfactant and permit identification additive used in commercial surfactant. This findings/identification will further enhance quality of synthesize surfactant.
- 2) It is also recommended Chemical Engineering Department can elongate Final Year Research Project (FYRP) course so this idea can be further attest with simulation besides experimental research only. Example of simulation which can be done on this research is simulation by pendant drop technique using MATLAB Application.[17]
- 3) It is also suggested University Technology of PETRONAS (UTP) can provide tensiometer such as DuNuoy Instrument and capillary viscometer, so that two important physical characteristic i.e. interfacial tension and viscosity can be compared.

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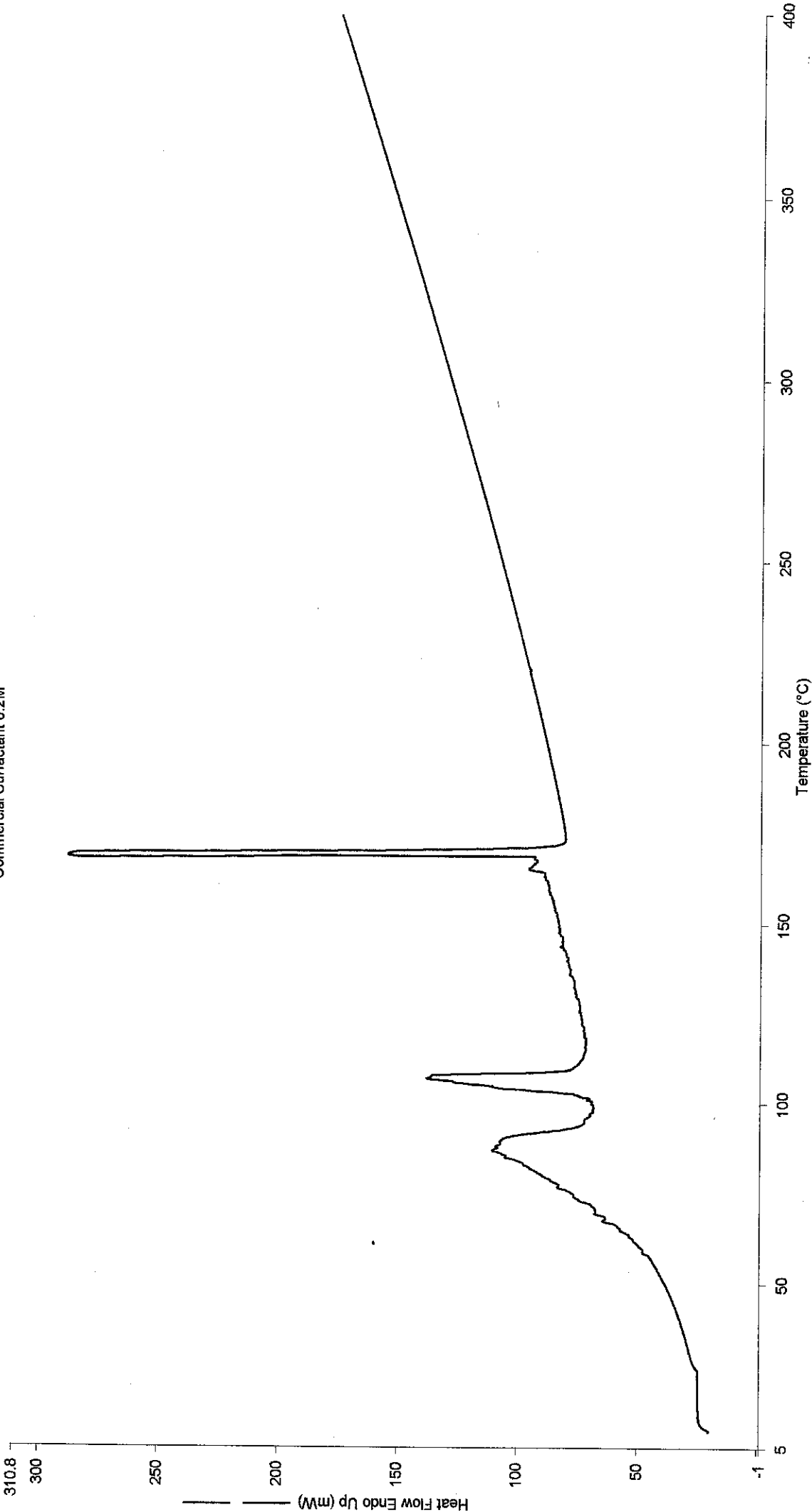
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APPENDICES

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Commercial Surfactant 0.2M

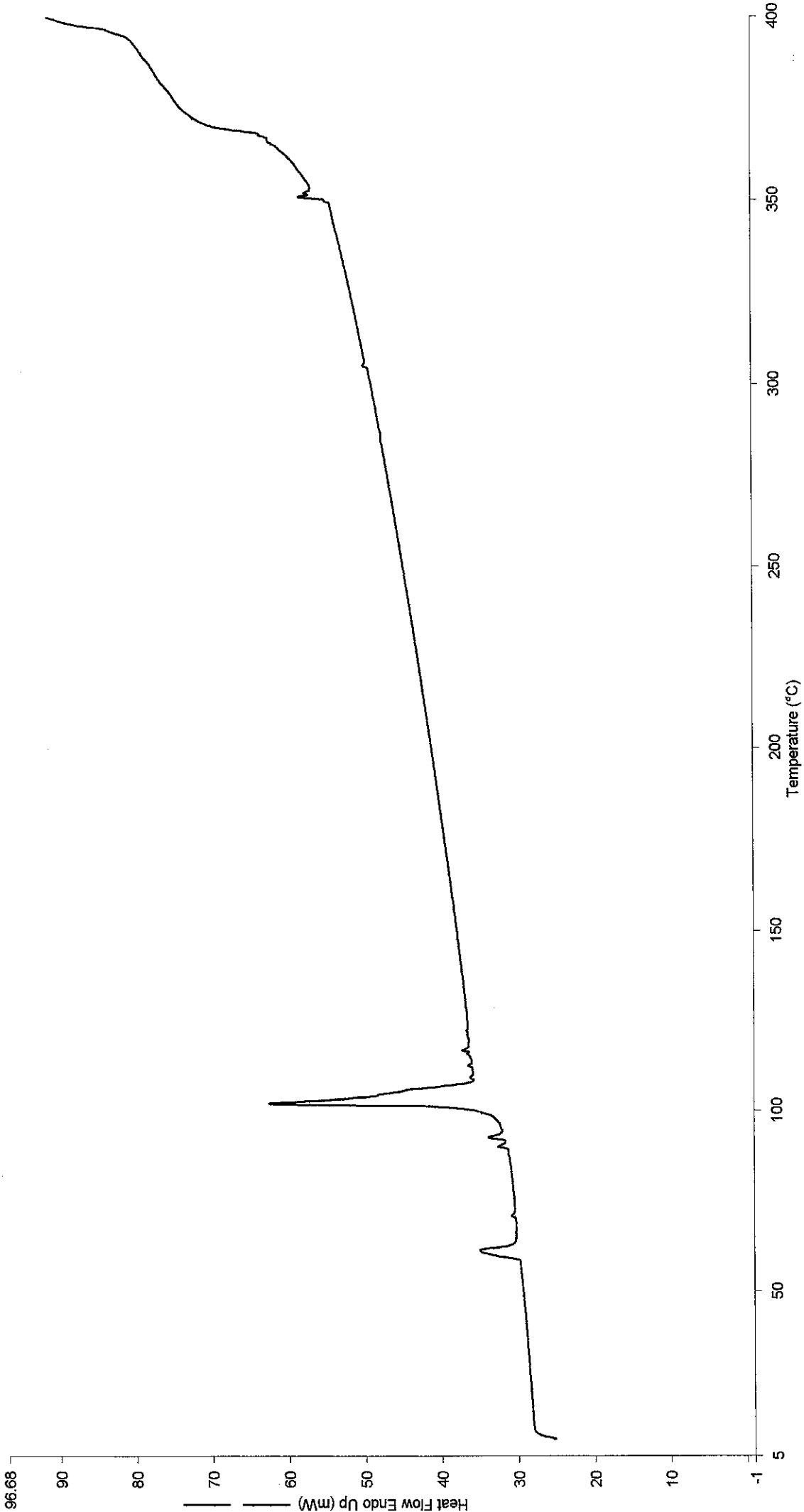


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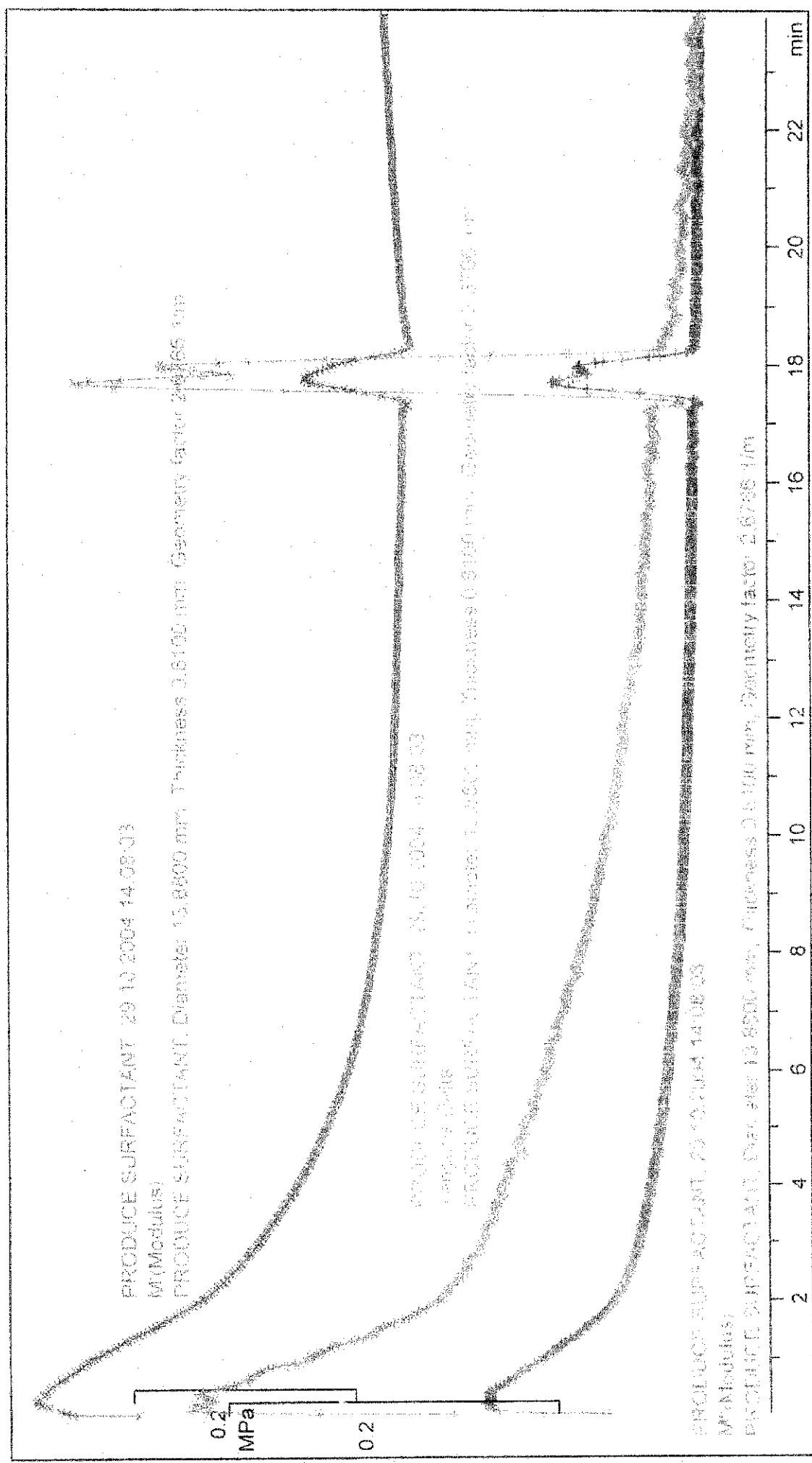
2) Heat from 10.00°C to 400.00°C at 10.00°C/min

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Sample ID: 7.100 mg
Total Points in Run: 3960

Produce Surfactant 0.2M



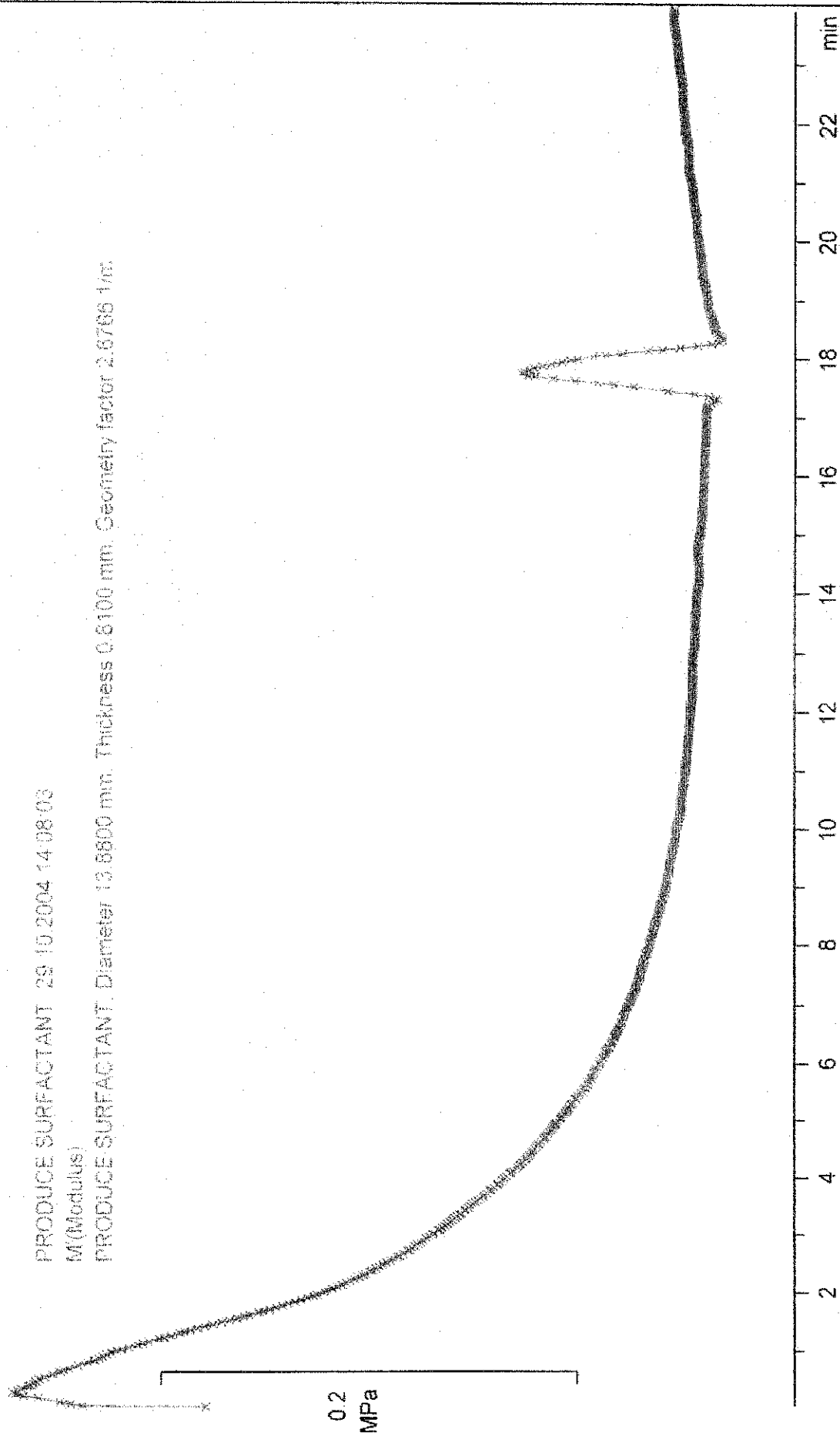
1) Hold for 1.0 min at 10.00°C 2) Heat from 10.00°C to 400.00°C at 10.00°C/min



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56	117	29.73	29.5	0.4477
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96	193	42.39	42.17	0.3819
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136	270	54.73	55	0.3414
144	285	57.13	57.5	0.335
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176	346	66.89	67.67	0.3138
184	361	69.31	70.17	0.3097
192	376	71.74	72.67	0.3057
200	392	74.33	75.33	0.3017
208	407	76.78	77.83	0.2987
216	422	79.23	80.33	0.2959
224	438	81.86	83	0.2926
232	453	84.34	85.5	0.2905
240	469	86.99	88.17	0.288
248	484	89.48	90.67	0.2858
256	499	91.98	93.17	0.284
264	514	94.47	95.67	0.2818
272	529	96.97	98.17	0.2799
280	544	99.47	100.7	0.2781
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296	575	104.7	105.8	0.2756
304	590	107.2	108.3	0.274
312	605	109.8	110.8	0.2729
320	622	112.6	113.7	0.2714
328	637	115.2	116.2	0.2707
336	652	117.7	118.7	0.2697

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376	727	130.5	131.2	0.2664
384	743	133.2	133.8	0.2658
392	758	135.8	136.3	0.2657
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464	896	159.7	159.3	0.2626
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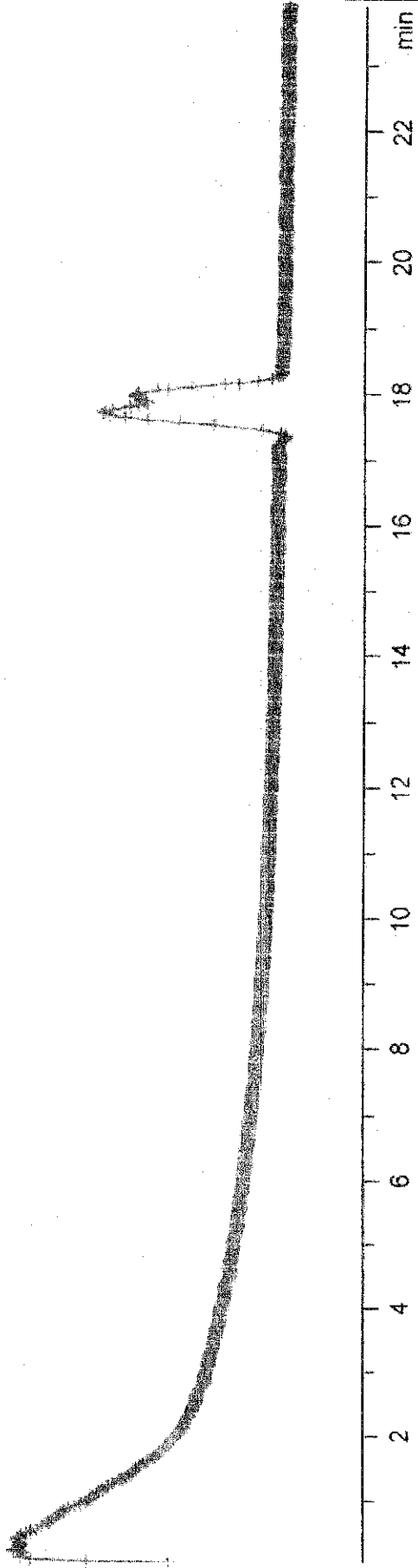
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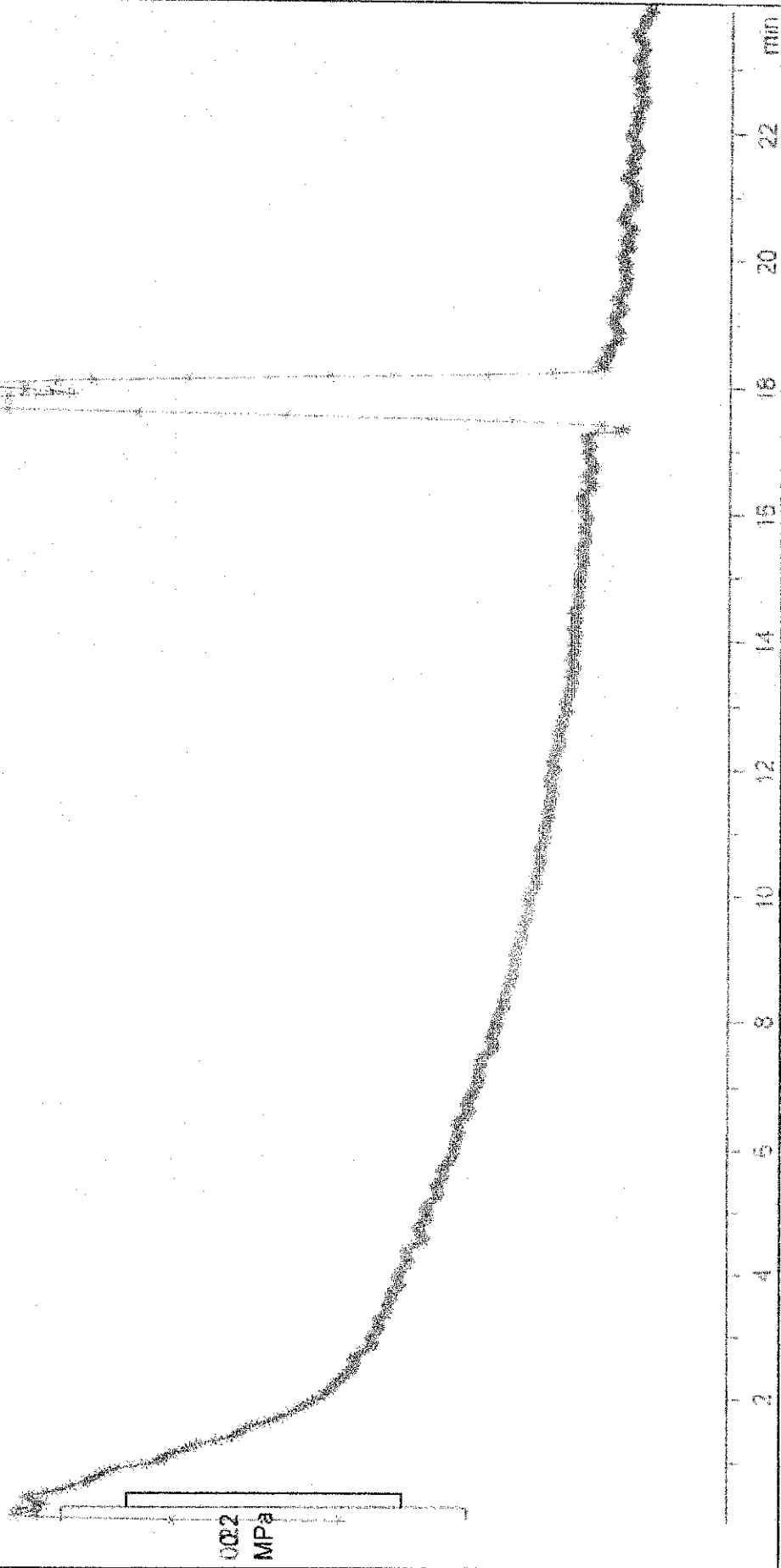
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200	392	74.33	75.33	0.1317
208	407	76.78	77.83	0.1308
216	422	79.23	80.33	0.127
224	438	81.86	83	0.1258
232	453	84.34	85.5	0.1191
240	469	86.99	88.17	0.119
248	484	89.48	90.67	0.1171
256	499	91.98	93.17	0.1144
264	514	94.47	95.67	0.1118
272	529	96.97	98.17	0.1094
280	544	99.47	100.7	0.1089
288	560	102.1	103.3	0.1051
296	575	104.7	105.8	0.1035
304	590	107.2	108.3	0.1019
312	605	109.8	110.8	0.1001
320	622	112.6	113.7	0.09774
328	637	115.2	116.2	0.09659
336	652	117.7	118.7	0.09416

344	667	120.3	121.2	0.0937
352	682	122.8	123.7	0.09212
360	697	125.4	126.2	0.09028
368	712	127.9	128.7	0.09137
376	727	130.5	131.2	0.09043
384	743	133.2	133.8	0.08689
392	758	135.8	136.3	0.08576
400	774	138.6	139	0.083
408	789	141.2	141.5	0.08255
416	805	143.9	144.2	0.08214
424	820	146.5	146.7	0.08102
432	835	149.1	149.2	0.08027
440	850	151.7	151.7	0.08015
448	865	154.3	154.2	0.08045
456	880	156.9	156.7	0.07766
464	896	159.7	159.3	0.07755
472	911	162.3	161.8	0.07583
480	926	164.9	164.3	0.0768
488	942	167.6	167	0.07484
496	957	170.2	169.5	0.07337
504	972	172.8	172	0.07597
512	988	175.6	174.7	0.07125
520	1003	178.2	177.2	0.07031
528	1018	180.9	179.7	0.07352
536	1033	183.5	182.2	0.0741
544	1052	186.8	185.3	0.2972
552	1067	189.4	187.8	0.347
560	1082	192.1	190.3	0.3194
568	1098	194.9	193	0.06485
576	1113	197.5	195.5	0.06359
584	1129	200.4	198.2	0.05756
592	1144	203	200.7	0.0615
600	1159	205.7	203.2	0.05889
608	1174	208.3	205.7	0.05498
616	1189	211	208.2	0.05593
624	1204	213.7	210.7	0.05778
632	1219	216.3	213.2	0.05656
640	1235	219.1	215.8	0.05576
648	1250	221.7	218.3	0.05339
656	1266	224.5	221	0.05058
664	1281	227.1	223.5	0.05376
672	1296	229.7	226	0.05219
680	1312	232.5	228.7	0.05186
688	1327	235.1	231.2	0.05086
696	1342	237.7	233.7	0.04915
704	1357	240.3	236.2	0.04929
712	1373	243	238.8	0.0492
720	1388	245.6	241.3	0.04966
728	1403	248.2	243.8	0.04678
736	1418	250.8	246.3	0.04741
744	1434	253.6	249	0.04277

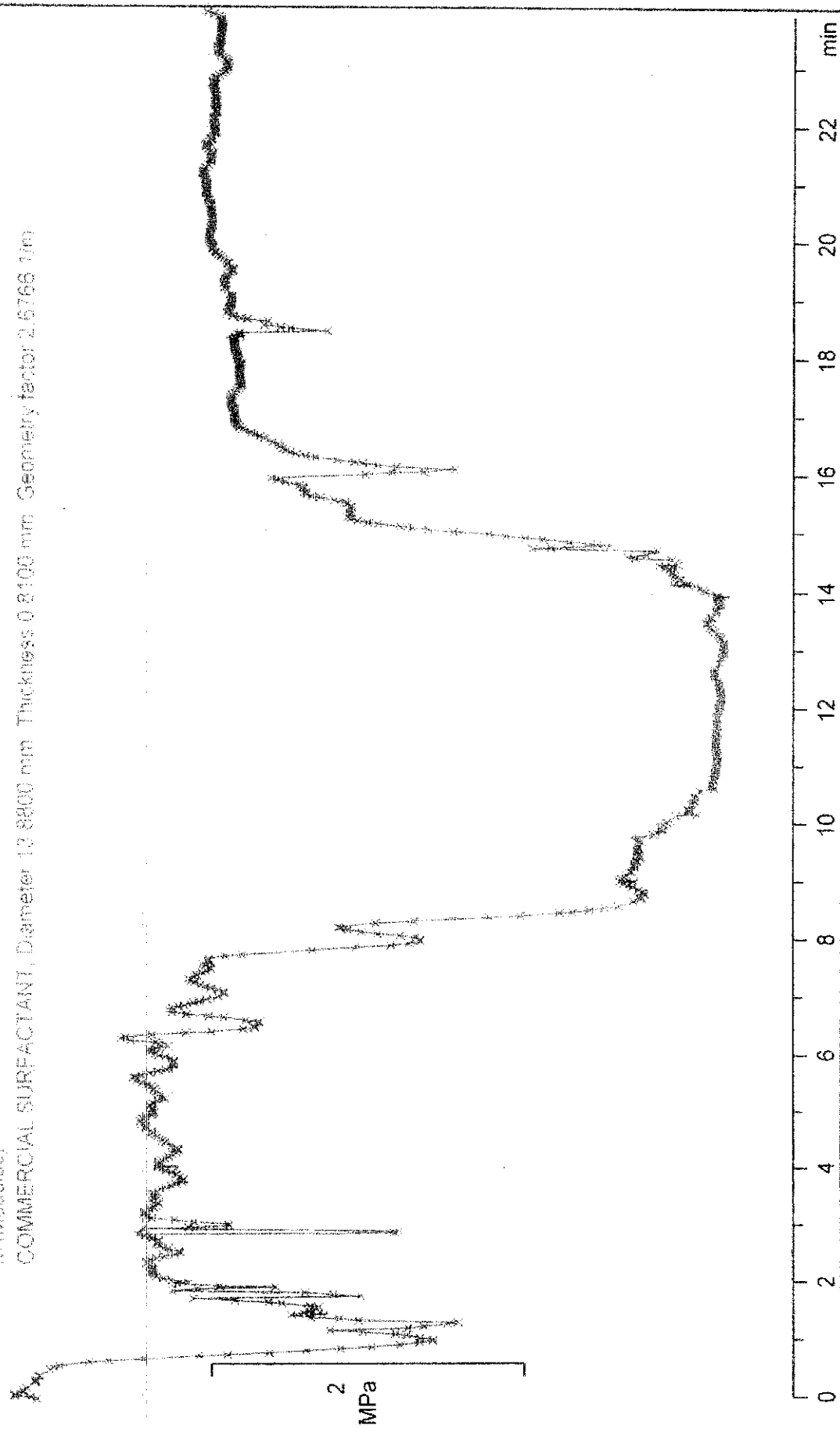
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RODUCE SURFACTANT, Diameter 13.8800 mm, Thickness 0.8100 mm, Geometry fa

COMMERCIAL SURFACTANT 20 10 2004 12:35:42

MM Modulus

COMMERCIAL SURFACTANT, Diameter 13.8800 mm Thickness 0.2100 mm Geometry factor 2.6766 1/m



Lab: METTLER

STAR® SW 8.01

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ve Name:

COMMERCIAL SURFACTANT, 29.10.2004 12:35:42

' (Modulus)

ve Values:

Index	Time [s]	Sample Temp [°C]	Ref. Temp [°C]	Value [MPa]
0	0	16.21	10	4.803
8	18	16.3	13	4.809
16	39	17.06	16.5	4.338
24	55	18.45	19.17	2.469
32	70	20.62	21.67	2.916
40	86	23.94	24.33	3.164
48	101	28.09	26.83	3.526
56	116	32.77	29.33	3.624
64	132	36.06	32	4.053
72	147	38.23	34.5	3.976
80	162	40.73	37	4.021
88	177	44.39	39.5	3.821
96	192	46.93	42	4.108
104	208	49.02	44.67	4.041
112	223	51.03	47.17	3.901
120	239	53.12	49.83	3.998
128	254	55.07	52.33	3.924
136	269	57.12	54.83	3.988
144	284	59.17	57.33	4.101
152	299	61.28	59.83	4.042
160	314	63.39	62.33	3.967
168	330	65.63	65	4.119
176	345	67.65	67.5	3.943
184	361	69.72	70.17	4.027
192	376	71.51	72.67	4.258
200	392	73.41	75.33	3.382
208	407	74.95	77.83	3.924
216	424	75.86	80.67	3.596
224	440	76.6	83.33	3.79
232	455	77.69	85.83	3.695
240	474	79.55	89	2.403
248	490	81.21	91.67	2.846
256	507	83.1	94.5	1.357
264	527	85.65	97.83	0.9011
272	542	88.03	100.3	1.05
280	559	90.99	103.2	0.9532
288	574	93.92	105.7	0.9393
296	595	98.56	109.2	0.7937
304	614	102.8	112.3	0.6209
312	635	100.5	115.8	0.4505
320	653	105.9	118.8	0.4451
328	672	111.3	122	0.4381
336	687	116.2	124.5	0.442

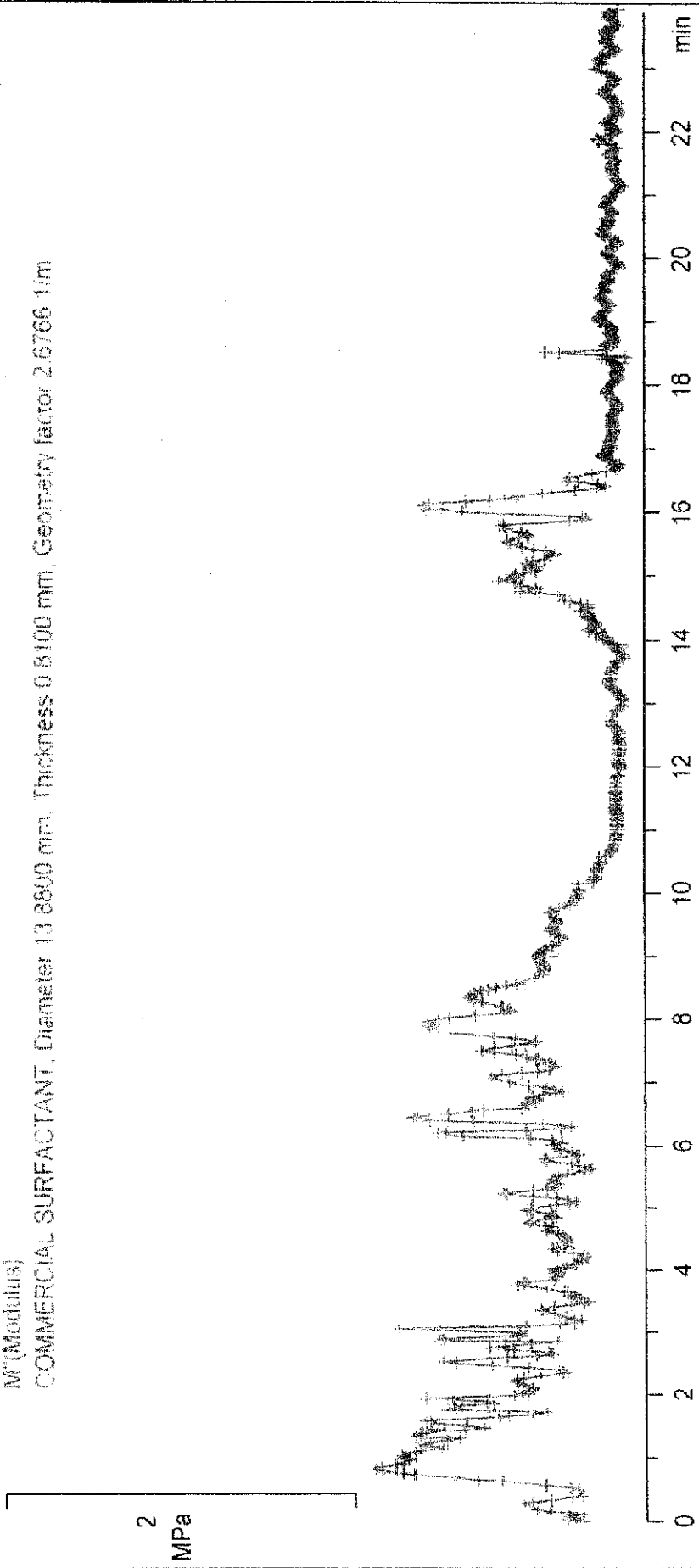
344	709	124	128.2	0.4339
352	729	130.9	131.5	0.41
360	746	137.1	134.3	0.4335
368	771	146.6	138.5	0.4072
376	791	153.4	141.8	0.4088
384	808	160.4	144.7	0.5028
392	826	167.8	147.7	0.4196
400	843	173.8	150.5	0.5457
408	858	177.8	153	0.7198
416	873	180.9	155.5	0.9599
424	890	183.5	158.3	1.384
432	905	185.2	160.8	2.46
440	920	186.5	163.3	2.783
448	936	187.5	166	3.034
456	955	188.2	169.2	3.295
464	972	189	172	2.759
472	988	190	174.7	3.238
480	1005	191.5	177.5	3.482
488	1020	192.9	180	3.535
496	1036	194.5	182.7	3.555
504	1051	196	185.2	3.488
512	1066	197.5	187.7	3.503
520	1081	199.2	190.2	3.517
528	1097	201	192.8	3.53
536	1112	202.8	195.3	3.341
544	1129	205	198.2	3.565
552	1144	207.1	200.7	3.561
560	1161	209.6	203.5	3.585
568	1176	211.9	206	3.579
576	1191	214.2	208.5	3.672
584	1206	216.5	211	3.691
592	1222	219	213.7	3.677
600	1238	221.6	216.3	3.691
608	1254	224.1	219	3.714
616	1269	226.5	221.5	3.738
624	1286	229.2	224.3	3.678
632	1302	231.8	227	3.698
640	1317	234.2	229.5	3.657
648	1332	236.6	232	3.652
656	1347	239.1	234.5	3.652
664	1362	241.6	237	3.675
672	1378	244.3	239.7	3.575
680	1393	246.8	242.2	3.632
688	1408	249.3	244.7	3.617
696	1424	252	247.3	3.611

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COMMERCIAL SURFACTANT, Diameter 13.8800 mm, Thickness 0.8100 mm, Geometry /m

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COMMERCIAL SURFACTANT Diameter 13.8800 mm, Thickness 0.8100 mm, Geometry factor 2.6766 1/m



Lab: METTLER

STAR® SW 8.01

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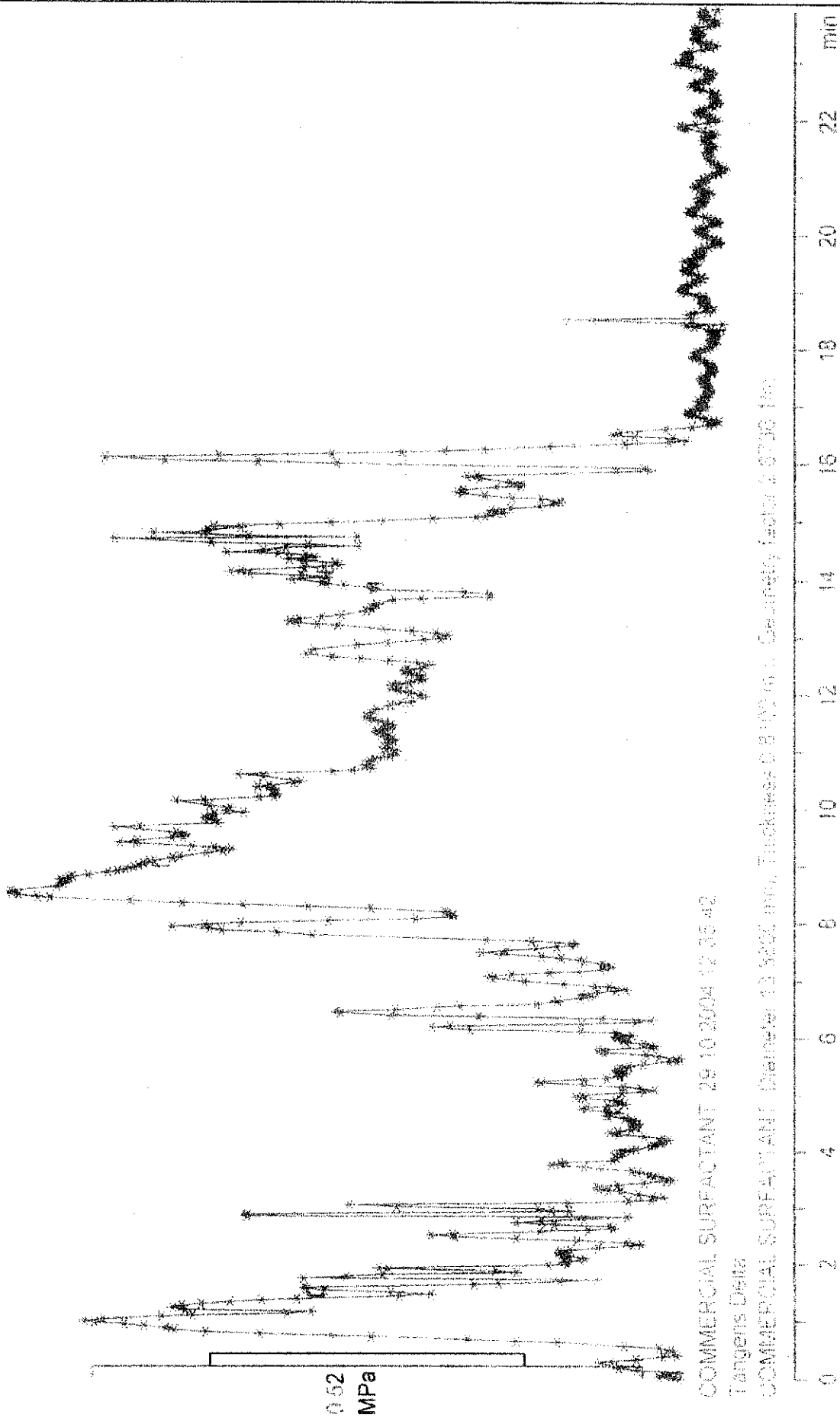
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16	39	17.06	16.5	0.9553
24	55	18.45	19.17	1.378
32	70	20.62	21.67	1.185
40	86	23.94	24.33	1.031
48	101	28.09	26.83	0.6373
56	116	32.77	29.33	1.249
64	132	36.06	32	0.7326
72	147	38.23	34.5	0.8714
80	162	40.73	37	0.7449
88	177	44.39	39.5	0.7183
96	192	46.93	42	0.3946
104	208	49.02	44.67	0.3383
112	223	51.03	47.17	0.6165
120	239	53.12	49.83	0.4911
128	254	55.07	52.33	0.3405
136	269	57.12	54.83	0.4366
144	284	59.17	57.33	0.6571
152	299	61.28	59.83	0.644
160	314	63.39	62.33	0.7997
168	330	65.63	65	0.4839
176	345	67.65	67.5	0.5566
184	361	69.72	70.17	0.5188
192	376	71.51	72.67	0.473
200	392	73.41	75.33	0.9846
208	407	74.95	77.83	0.5713
216	424	75.86	80.67	0.8739
224	440	76.6	83.33	0.5976
232	455	77.69	85.83	0.6749
240	474	79.55	89	1.197
248	490	81.21	91.67	0.8018
256	507	83.1	94.5	0.8882
264	527	85.65	97.83	0.5643
272	542	88.03	100.3	0.5863
280	559	90.99	103.2	0.4708
288	574	93.92	105.7	0.496
296	595	98.56	109.2	0.3707
304	614	102.8	112.3	0.2712
312	635	100.5	115.8	0.2125
320	653	105.9	118.8	0.1518
328	672	111.3	122	0.1454
336	687	116.2	124.5	0.147

344	709	124	128.2	0.1406
352	729	130.9	131.5	0.1339
360	746	137.1	134.3	0.1322
368	771	146.6	138.5	0.148
376	791	153.4	141.8	0.156
384	808	160.4	144.7	0.1759
392	826	167.8	147.7	0.1116
400	843	173.8	150.5	0.2264
408	858	177.8	153	0.2961
416	873	180.9	155.5	0.348
424	890	183.5	158.3	0.6915
432	905	185.2	160.8	0.6085
440	920	186.5	163.3	0.501
448	936	187.5	166	0.6525
456	955	188.2	169.2	0.3418
464	972	189	172	0.7851
472	988	190	174.7	0.3628
480	1005	191.5	177.5	0.1405
488	1020	192.9	180	0.17
496	1036	194.5	182.7	0.16
504	1051	196	185.2	0.1748
512	1066	197.5	187.7	0.1627
520	1081	199.2	190.2	0.1636
528	1097	201	192.8	0.1438
536	1112	202.8	195.3	0.2022
544	1129	205	198.2	0.1821
552	1144	207.1	200.7	0.2424
560	1161	209.6	203.5	0.2382
568	1176	211.9	206	0.1923
576	1191	214.2	208.5	0.1315
584	1206	216.5	211	0.1953
592	1222	219	213.7	0.2263
600	1238	221.6	216.3	0.191
608	1254	224.1	219	0.1833
616	1269	226.5	221.5	0.1194
624	1286	229.2	224.3	0.1731
632	1302	231.8	227	0.1673
640	1317	234.2	229.5	0.1685
648	1332	236.6	232	0.1722
656	1347	239.1	234.5	0.145
664	1362	241.6	237	0.172
672	1378	244.3	239.7	0.2634
680	1393	246.8	242.2	0.1831
688	1408	249.3	244.7	0.195
696	1424	252	247.3	0.1528

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COMMERCIAL SURFACTANT, Diameter 13.8800 mm, Thickness 0.8100 mm, Geometr
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Lab: METTLER

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COMMERCIAL SURFACTANT, 29.10.2004 12:35:42

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Index	Time [s]	Sample Temp [°C]	Ref. Temp [°C]	Value []
0	0	16.21	10	0.073
8	18	16.3	13	0.1337
16	39	17.06	16.5	0.2202
24	55	18.45	19.17	0.5582
32	70	20.62	21.67	0.4063
40	86	23.94	24.33	0.3259
48	101	28.09	26.83	0.1807
56	116	32.77	29.33	0.3447
64	132	36.06	32	0.1807
72	147	38.23	34.5	0.2192
80	162	40.73	37	0.1853
88	177	44.39	39.5	0.188
96	192	46.93	42	0.09605
104	208	49.02	44.67	0.08372
112	223	51.03	47.17	0.158
120	239	53.12	49.83	0.1229
128	254	55.07	52.33	0.08678
136	269	57.12	54.83	0.1095
144	284	59.17	57.33	0.1603
152	299	61.28	59.83	0.1593
160	314	63.39	62.33	0.2016
168	330	65.63	65	0.1175
176	345	67.65	67.5	0.1412
184	361	69.72	70.17	0.1288
192	376	71.51	72.67	0.1111
200	392	73.41	75.33	0.2911
208	407	74.95	77.83	0.1456
216	424	75.86	80.67	0.243
224	440	76.6	83.33	0.1577
232	455	77.69	85.83	0.1827
240	474	79.55	89	0.4979
248	490	81.21	91.67	0.2818
256	507	83.1	94.5	0.6547
264	527	85.65	97.83	0.6262
272	542	88.03	100.3	0.5583
280	559	90.99	103.2	0.4939
288	574	93.92	105.7	0.528
296	595	98.56	109.2	0.467
304	614	102.8	112.3	0.4367
312	635	100.5	115.8	0.4717
320	653	105.9	118.8	0.341
328	672	111.3	122	0.3318
336	687	116.2	124.5	0.3325

344	709	124	128.2	0.3241
352	729	130.9	131.5	0.3266
360	746	137.1	134.3	0.305
368	771	146.6	138.5	0.3635
376	791	153.4	141.8	0.3816
384	808	160.4	144.7	0.3499
392	826	167.8	147.7	0.2659
400	843	173.8	150.5	0.4149
408	858	177.8	153	0.4113
416	873	180.9	155.5	0.3625
424	890	183.5	158.3	0.4996
432	905	185.2	160.8	0.2473
440	920	186.5	163.3	0.18
448	936	187.5	166	0.215
456	955	188.2	169.2	0.1037
464	972	189	172	0.2846
472	988	190	174.7	0.1121
480	1005	191.5	177.5	0.04034
488	1020	192.9	180	0.04809
496	1036	194.5	182.7	0.04499
504	1051	196	185.2	0.05012
512	1066	197.5	187.7	0.04644
520	1081	199.2	190.2	0.04651
528	1097	201	192.8	0.04075
536	1112	202.8	195.3	0.06054
544	1129	205	198.2	0.05108
552	1144	207.1	200.7	0.06806
560	1161	209.6	203.5	0.06645
568	1176	211.9	206	0.05374
576	1191	214.2	208.5	0.03582
584	1206	216.5	211	0.05291
592	1222	219	213.7	0.06153
600	1238	221.6	216.3	0.05174
608	1254	224.1	219	0.04935
616	1269	226.5	221.5	0.03195
624	1286	229.2	224.3	0.04706
632	1302	231.8	227	0.04524
640	1317	234.2	229.5	0.04608
648	1332	236.6	232	0.04715
656	1347	239.1	234.5	0.0397
664	1362	241.6	237	0.0468
672	1378	244.3	239.7	0.07367
680	1393	246.8	242.2	0.05041
688	1408	249.3	244.7	0.05392
696	1424	252	247.3	0.0423

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COMMERCIAL SURFACTANT, Diameter 13.8800 mm, Thickness 0.8100 mm, Geometr
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